

The Journal *of the* SOCIETY OF DYERS AND COLOURISTS

Volume 69 Number 9

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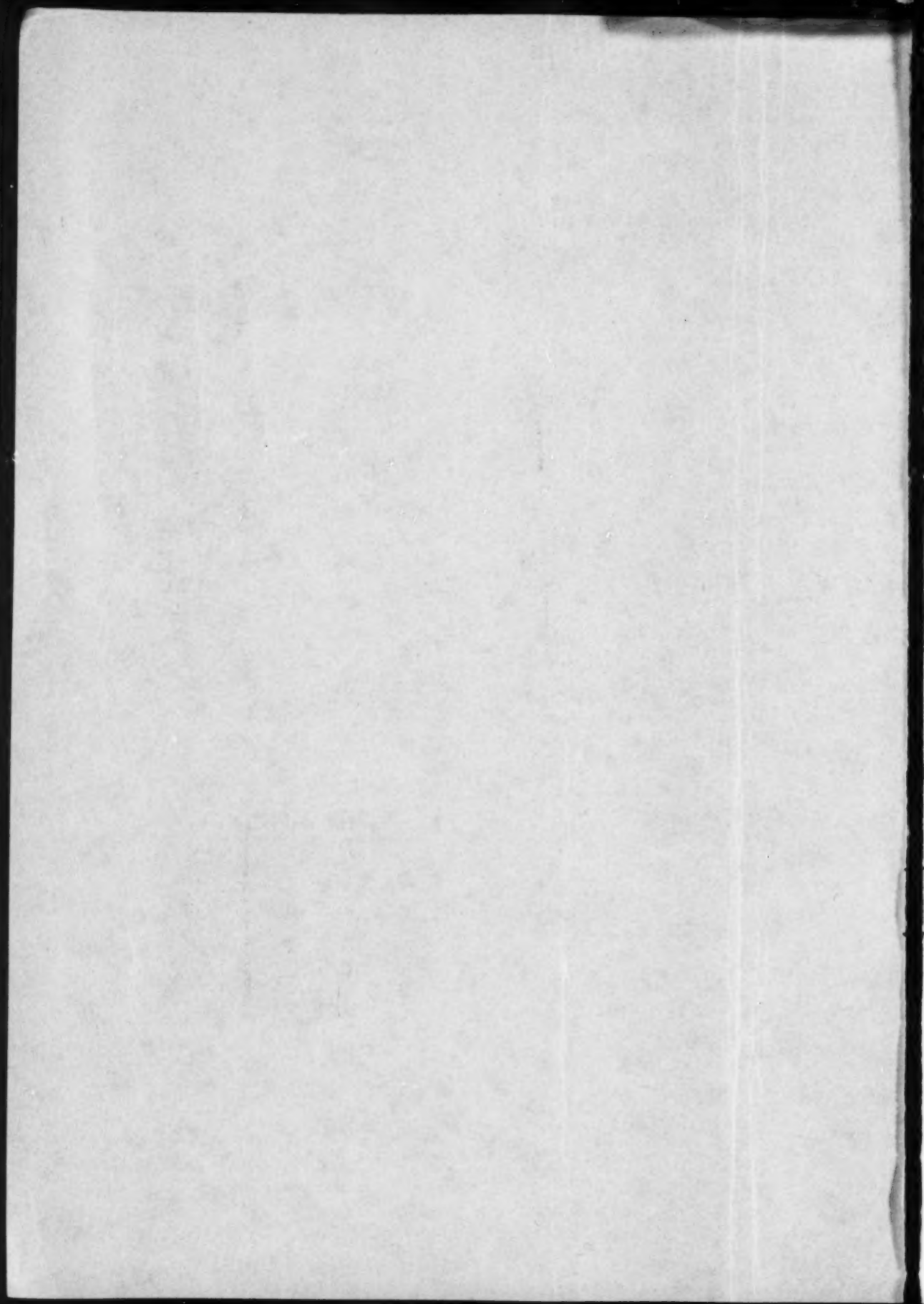


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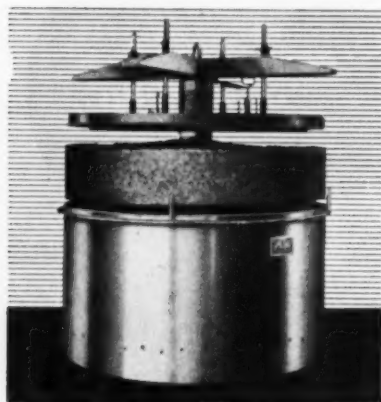
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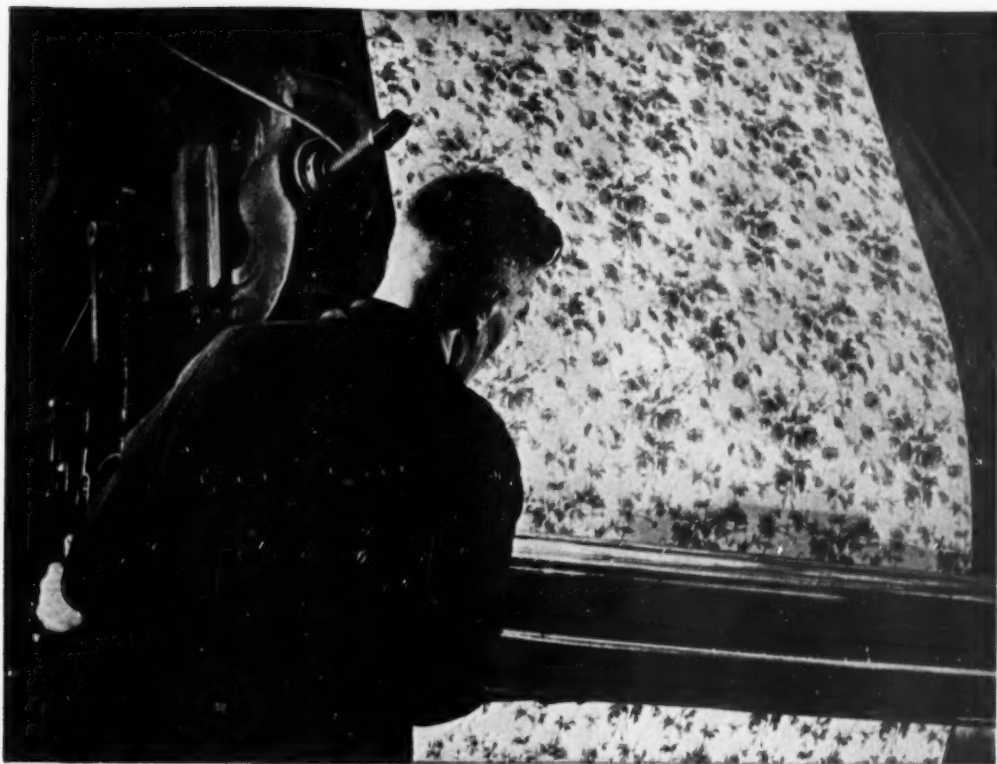


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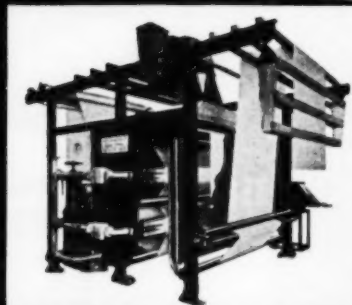
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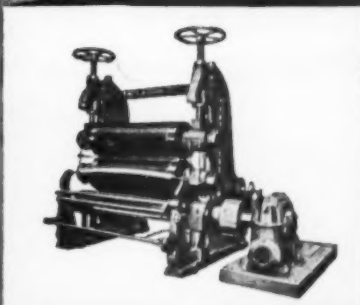
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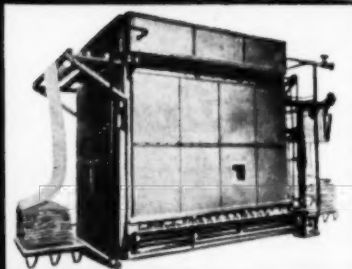
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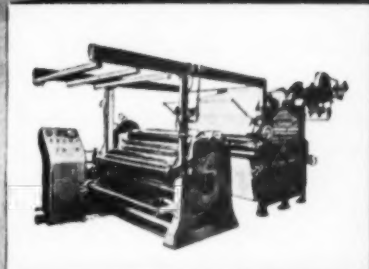
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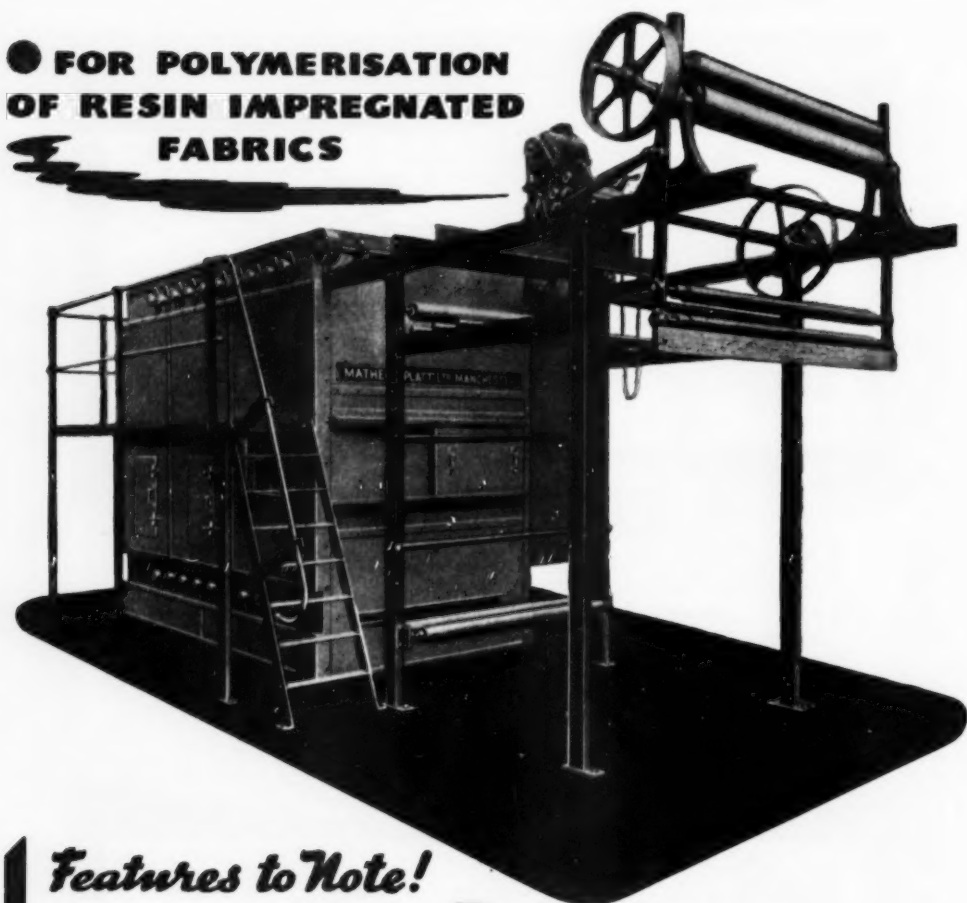
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FORTHCOMING MEETINGS OF THE SOCIETY

SCOTTISH SECTION

All Meetings in St. Enoch Hotel, Glasgow, at 7.0 p.m., unless otherwise stated

- 1953
 Tuesday 29th Sept. Dr. I. S. M. Walls (I.C.I.). *The Dyeing and Finishing of Fabrics containing the Newer Synthetic Fibres*
 Tuesday 27th Oct. Dr. G. H. Lister (Sandoz Products Ltd.). *The Migration Properties of Acid and Chrome Dyestuffs*
 Tuesday 17th Nov. J. S. Ingham, Esq., M.Sc., F.R.I.C. (Marks and Spencer Ltd.). *Problems of Colour Fastness and Finish*
 Thursday 10th Dec. Dr. J. F. Gaunt (Messrs. Patons & Baldwins Ltd.), Scottish Woollen Technical College, Galashiels. *A discussion on the Relative Merits of Different Methods of Applying Chrome Dyes*
 Tuesday 15th Dec. Prof. P. D. Ritchie. *Links between the Textile and Plastics Industries*

MIDLANDS SECTION

Except when stated otherwise, Lecture Meetings commence at 7.0 p.m.

- 1953
 Wednesday 30th Sept. C. O. Clark, Esq., F.T.I. *Some Authentic Records of the Craft of Dyeing*. College of Technology, Leicester
 Thursday 22nd Oct. S. Burgess, Esq., A.M.C.T. *Economic and Technical Difficulties in meeting Fastness Requirements*. The College, Loughborough
 Tuesday 3rd Nov. D. N. Marvin, Esq., A.R.I.C., A.T.I. (Joint meeting with Hinckley Textile Society). *Some Properties of Terylene*. College of Further Education, Hinckley. 7.15 p.m.
 Wednesday 18th Nov. H. R. Hadfield, Esq., M.Sc. *The Dyeing of Caprolactam Fibres (Perlon etc.)*. Midland Hotel, Derby
 Saturday 21st Nov. LADIES' EVENING — DINNER DANCE, Black Boy Hotel, Nottingham
 Wednesday 2nd Dec. R. W. Speke, Esq., B.Sc. *A Study of Variables in Padding*. Black Boy Hotel, Nottingham
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 Wednesday 20th Jan. J. Payne, Esq., B.Sc. *Silicon Chemicals in Textile Finishing*. College of Technology, Leicester
 Wednesday 24th Feb. Douglas Haigh, Esq., A.T.I. *Some recent researches in the Dyeing of Felt*. Masonic Hall, Nuneaton
 Thursday 4th March R. F. Wilson, Esq. (B.C.C.) (Joint meeting with the Nottingham Textile Society). *Colour*. Gas Theatre, Nottingham
 Wednesday 17th March G. H. Lister, Esq., B.Sc., Ph.D. *The Migration Properties of Acid and Chrome Dyes*. Victoria Station Hotel, Nottingham
 Friday 26th March MIDLANDS SECTION DINNER. King's Head Hotel, Loughborough
 Wednesday 7th April ANNUAL GENERAL MEETING OF SECTION. J. A. Potter, Esq., M.A. *Dyeing and Finishing Synthetic Fibres in the Hosiery Industry*. King's Head Hotel, Loughborough

LONDON SECTION

All Meetings will be held at the Royal Society, Burlington House, Piccadilly, London W.1, at 6.0 p.m. unless otherwise stated

- 1953
 Friday 2nd Oct. C. R. M. Oehlcke (Newcol Ltd.). *The Use of Organic Pigments in Modern Plastics*
 Friday 6th Nov. Messrs. B. Kramrisch and A. Bratt (Clayton Aniline Co. Ltd.). *Problems of the Garment Dyer and Finisher, including the Dyeing of Buttons*

LONDON SECTION (continued)

- Thursday 3rd Dec. Alec B. Hunter (Warner & Sons Ltd.). *Design and Colour*
 1954
 Thursday 7th Jan. Dr. G. T. Douglas (I.C.I. Ltd.). *The Dyeing of Synthetic Fibres*
 Friday 5th Feb. C. P. Tattersfield (Courtaulds Ltd.). *Dyeing and Finishing in relation to Use-Development Work*
 Friday 5th March *The London Lecture*. Subject, Speaker and venue to be given

MANCHESTER SECTION

Unless otherwise stated, meetings take place at the Textile Institute, 10 Blackfriars Street, Manchester 3, and commence at 6.30 p.m.

- 1953
 Friday 16th Oct. F. Ward, Esq. (Courtaulds Ltd.). *The Principles and Practice of Flameproofing Textiles*
 Friday 20th Nov. LADIES' EVENING *How do I know what to buy?* Commences at 7.0 p.m. Details will be announced later
 Friday 18th Dec. Details to be announced later
 1954
 Friday 15th Jan. S. Blackburn Esq., and M. R. Fox, Esq. (I.C.I. Ltd., Dyestuffs Divn.). *The Behaviour of Leuco Vat Dyes above 100°C.*

WEST RIDING SECTION

Meetings held at the Victoria Hotel, Bradford, at 7.15 p.m. unless otherwise stated

- 1953
 Friday 16th Oct. SUPPER AND SMOKER
 Thursday 29th Oct. Sir Ernest Goodale, C.B.E., M.C. *Ancient and Modern Textile Production in London and the Home Counties*

NORTHERN IRELAND SECTION

All Meetings with the exceptions of "Ladies' Evening" and "du Pont Story" to be held in Royal Avenue Hotel, Belfast, at 7.30 p.m.

- 1953
 Thursday 8th Oct. R. W. Speake, Esq. (I.C.I. Ltd.). *Variables in Padding Processes*
 Wednesday 28th Oct. LADIES' EVENING, to be held in Thompson's Restaurant, Belfast, at 7.30 p.m.
 Friday 6th Nov. S. J. Hill, Esq. (United Chrometanners Ltd.). *Production and Dyeing of Leather*
 Two films will be shown *Romance of Leather and Hide to Sole*
 Friday 4th Dec. J. V. Summersgill, Esq. (Geigy Co. Ltd.). *Some Aspects of the Chemistry and Textile Uses of Sequestering Agents*
 Thursday 10th Dec. *du Pont Story*. To be held in Thompson's Restaurant, Belfast, at 7.30 p.m. This is a colour/sound film. (Joint Meeting with Textile Institute)

- 1954
 Friday 8th Jan. C. P. Tattersfield, Esq. (Courtaulds Ltd.). *Developing New Uses for Rayon*. (Joint meeting with Textile Institute)

- Friday 5th Feb. W. Ford-Kirkpatrick, Esq. *Putting the Colour into Photography*
 Friday 5th March J. Potter, Esq. (Clayton Aniline Co. Ltd.). *Special Finishes for Textiles and Their Evaluation*. (Joint meeting with Foremen Dyers Guild)

- Late March or early April ANNUAL GENERAL MEETING AND DINNER. (Details later)

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring general information regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1-6 of the January 1953 and pages 229-232 of the July 1953 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (Telephone Bradford 25138-9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

The Dyeing of Viscose Rayon at High Temperatures *K. Butterworth*

The Textile Trade and the Newer Fibres *F. H. Clayton*

The Heat Setting of Terylene Polyester Filament Fabrics in relation to Dyeing and Finishing *D. N. Mavin*

Studies in the Printing of Terylene Polyester Fibre *A. G. H. Michie*

Fugitive Tinting with particular reference to Celafibre
H. C. Olpin and A. J. Wesson

The Uses of Microscopy in Textile Dyeing and Finishing
G. G. Taylor and J. C. Brown

COMMUNICATIONS

The Reaction between Wool and Nickelammonium Hydroxide.

II—The Supercontraction of Wool Fibres in Solutions of Nickelammonium Hydroxide
J. W. Bell and C. S. Whewell

Studies in the Fundamental Processes of Textile Printing.

VI—The Transfer of Disperse and Water-soluble Dyes to Nylon during Steaming
E. H. Daruwalla and H. A. Turner

Absorptiometric Colorimetry in the Textile Laboratory
C. H. Giles and J. S. Shaw

Observations on Some Commercial Colour Matching Lamps
J. C. Guthrie and P. H. Oliver

Further Observations on the Effects of Evaporating Water from Cotton Cellulose
G. W. Madaras and H. A. Turner

Some Experiments on the Over-dyeing of Nylon
C. D. O'Briain and R. H. Peters



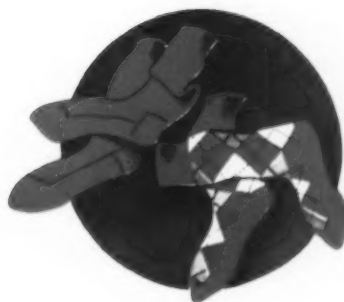
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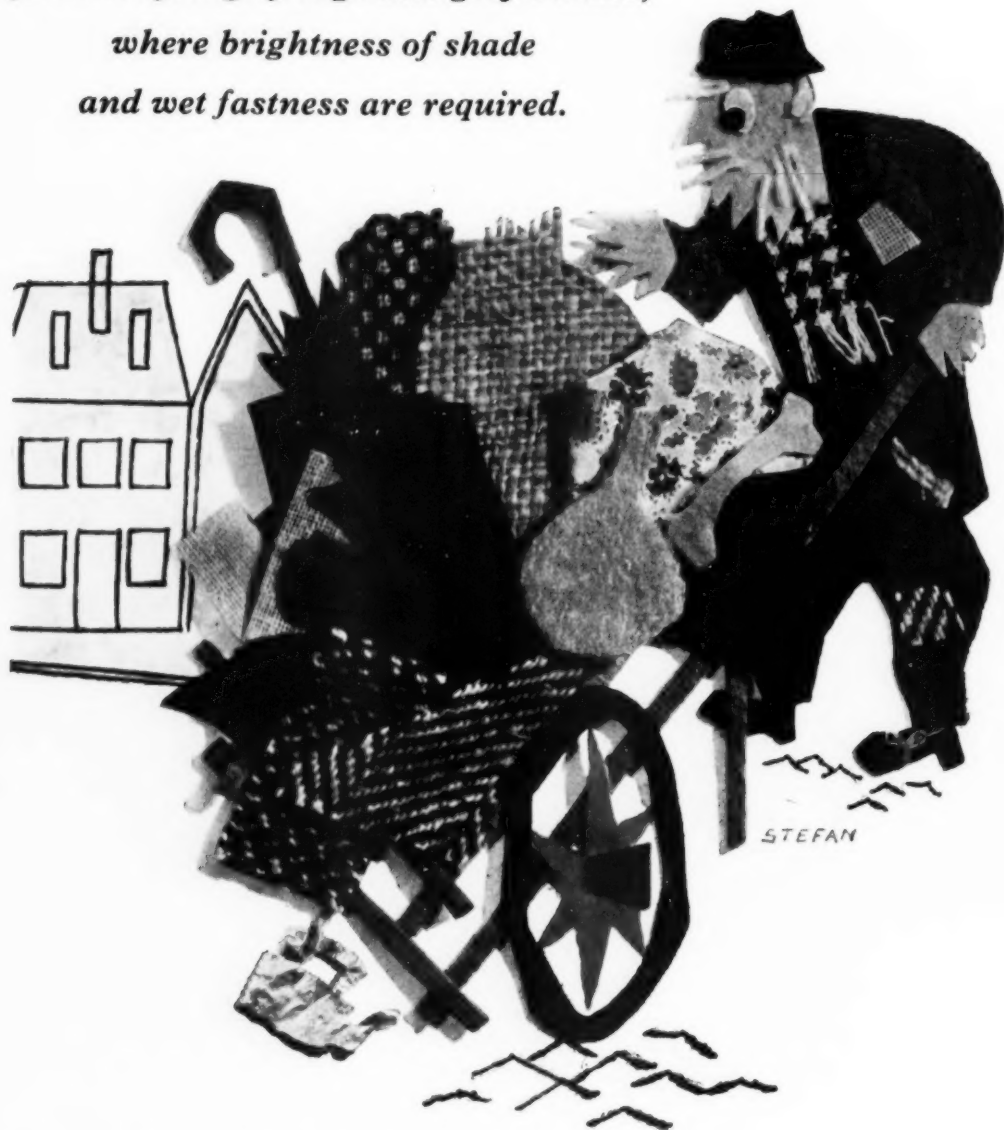


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THE JOURNAL

OF THE

Society of Dyers and Colourists

Volume 69 Number 9

SEPTEMBER 1953

Issued Monthly

Proceedings of the Society

Ancient and Modern Textile Production in London and the Home Counties

Sir ERNEST GOODALE

*Meeting of the London Section held at the Waldorf Hotel, Aldwych, on 6th March 1953,
Mr. G. Wood in the chair*

INTRODUCTION

The title of this lecture is not only long but also of vast import. It comprises much of London's long history from Roman times to the products of the haute couture of to-day, the history of many of the Craft Guilds or Livery Companies, and the growth of the City wholesale houses and the clothing trade. In 1935, for example, there were over 10,000 workrooms making clothing and employing less than ten employees in the County of London alone. Not content with this, I have added *and the Home Counties* to the title. This brings in weaving activities in Essex and printing activities in Surrey and Kent. I do not propose, however, to deal with clothing, only with piece goods. I feel my task is not to trace the history of our subject in detail but to treat it as an introduction to perhaps a series of lectures of the future, which will take in turn sections of our great subject and deal with each in detail.

Let me begin by painting with a broad brush the general outlines of our subject on a large canvas, and to do so coherently necessitates an abandonment of any effort at chronology. I may sketch the history of one of the Livery Companies to the present day, and then go back to the Middle Ages for a glimpse of another facet of our subject. I hope, however, that this will not prove too confusing.

Let us then start by reminding ourselves that "Man is a Weaver", and wherever men have congregated since the days of the Lake Dwellers they have tried to make themselves clothes. By the time the Romans began to make Londinium a town of some importance, figured weaving—not just plain weaving—had already reached a very high standard in China, Egypt, Mesopotamia, Crete and early Greece, then in later Greece and Rome.

In such books as I have studied I have found little reference as such to London as a textile centre. It all seems rather taken for granted. There is a book with the interesting title *Textile London* which was published by *The Drapers' Record*. It is undated, but by the illustrations I should guess its date as in the early 1890s. On dipping into this book with the helpful title, however, I found it to be more of a description of the City of London as such in the wards and parishes where textile firms were then to be found than a description of London's textile activities! There are many interesting facts in it, however, and one is reminded of such textile names as Wardrobe Court in Doctors Commons, Weavers' Hall and the Wool Exchange in Basinghall Street, and Distaff Lane off Cannon Street. We shall be dipping into this book again later.

THE CITY LIVERY COMPANIES

No account of textile London could properly be given without reference to the story of the Craft Guilds or Livery Companies. There are to-day twelve great Companies, of which five—Mercers, Drapers, Merchant Taylors, Haberdashers, and Clothworkers—relate to textiles and clothing. In addition there are sixty-seven lesser Livery Companies, of which the Weavers' Company is indeed the very oldest of all the Companies, great and small.

In addition to the Weavers the following seven Companies all have to do with the textile industry in some form—Broderers, Dyers (one very near the Society's heart), Feltmakers, Framework Knitters, Girdlers, Needlemakers, and Woolmen. On the fringe may be mentioned Glovers and Gold and Silver Wyre Drawers.

Among the eleven Companies now extinct may also be noted the Silk-throwers, Silkmen,

Pinmakers, Hatbandmakers, and Starchmakers. (It is not altogether surprising that one of the extinct Companies is that of the Longbow Stringmakers!)

Out of a total, then, of ninety current and extinct Livery Companies, no less than twenty are or were directly or indirectly concerned with the textile industry and trades. There is so much of interest in these Guilds that it is necessary to say something about them.

The reason that the origin of each and every guild is obscure is that they came into existence without special ceremony and had been carrying on their good work for many years before we first hear of them in the twelfth and thirteenth centuries.

There can be little doubt that the development of the guilds at this period was stimulated and inspired by foreigners from the highly organised Continental cities, who brought with them novel and progressive business methods which inspired the English craftsmen with a desire to improve their trade organisation. Association with the Duchy of Normandy led to extension of commerce with other parts of Europe, and the rapid growth of trade brought existing guilds into prominence and encouraged the formation of others.

It can be readily understood that the feelings of brotherhood and mutual help and esteem engendered by the guilds must have been highly prized in a medieval community. The fact of being a member of a Worshipful Company gave a dignity and sense of importance to the old-world trader. It placed the man of commerce on a high level, and indeed the doctrine of the "dignity of labour" never had stouter champions than the medieval craftsmen.

The older guilds were rarely *founded* merely for the protection of trade. They were formed by groups of neighbours for the purpose of promoting social and religious intercourse.

In medieval London persons engaged in the same trade lived in the same quarter of the city. For instance, the Tailors were in Birch Lane. What more natural than that these traders, closely related in commercial rivalry by day and in friendly intercourse in the evening, should unite into semi-religious fraternities for "the support of the body and salvation of the soul"? The motto adopted by the guilds in many instances follows the example of the City Corporation and asks for the blessing or guidance of the Almighty. The Mercers' motto is *Honor Deo*, and that of the Weavers Company, "Weave Truth with Trust".

One and all still appoint honorary chaplains, and the attendance at special service in one of the City churches, which has a traditional connection with the Guild, is often a prominent feature in the ceremonial attached to the installation of the Master of each Company.

The central figure of the guild organisation in all instances and at all stages of its development was the master craftsman owning the instruments of production and selling the product. The journeyman was subordinated from the outset to the master, but the two were bound together by

community of interests, and were divided by no social barriers. The industrious apprentice could always hope to marry the merchant's daughter.

The guild was neither a trade union nor an employers' association: it was designed to represent the three distinct and often antagonistic interests of the employer, the workman, and the consumer. Three outstanding features of the old guilds were benevolence, arrangements for the burial of members, and provision for the future by means of bequests, which are the foundation of much of the wealth of the City Companies to-day.

Several of the old Charters of the Livery Companies refer to the *art and mystery* of the particular craft practised. I always imagined this word *mystery* to refer to the skill of each craftsman being a mystery to the uninformed layman; but my researches seem to confirm that the word is really a variant of the word *mastery*, and refers to the competence of the worker and not to the secret intricacies of his craft. It may properly be spelt *mistry*.

THE WEAVERS COMPANY

It has been said that, if the members of the Founders Company claim their descent from Tubal Cain, the first artificer in metals, the Weavers have an equal right to trace their lineage to Naamah, his sister. The Fellowship can certainly claim to be the most ancient of the existing Craft Guilds, as there is evidence that a Fraternity of Weavers existed in Saxon times. The Company is in possession of a Charter granted by Henry II, confirming a previous Charter granted by Henry I. The Charter is undated, but is attributed to the year 1155.

By the Charters of Henry I and II, it was granted to the Weavers of London to have their Guild in London, and that none should intermeddle in their mystery within the City, or in Southwark, or in other places appertaining to London, except he were a member of their Guild. In return for its privileges the Fraternity had to pay to the King an annual rent or *Ferma Gildæ* of 2 marks of gold. Some indication of the date of the first incorporation of the Weavers, under Henry I, is to be gathered from the fact that the payment of the *Ferma Gildæ* is duly recorded in the earliest Pipe Roll, preserved at the Records Office, and generally attributed to the year 1130.

The Weavers' Guild, now, therefore, over 820 years old, became so powerful that it came into conflict with King John and was suppressed.

The Fraternity, however, bobbed up again in the next reign, and Henry III confirmed its old Charters.

The Company could not at first get on with the City Corporation, but the two bodies patched up their differences, and at the beginning of the fourteenth century the Weavers submitted to the jurisdiction of the Mayor "to determine such matters touching the craft as could not be determined by the Guild Court".

In the reign of Edward III the English weavers were confronted with more serious rivals than the civic authorities. Foreign weavers were encouraged

to immigrate, and not only expressly exempted from the necessity of joining the native Guild but actually granted the benefit of independent incorporation. From 1372 the Flemish and Brabant weavers, and from 1415 a new Guild of Linen Weavers, yearly presented their officers to the Mayor and Aldermen, side by side with those of the original Guild. The disputes between the native and alien Guilds, after lasting nearly two centuries, were finally terminated by the fusion of the two bodies, confirmed by the Mayor and Aldermen in 1498.

During the seventeenth and eighteenth centuries the craft of weaving became highly specialised and incorporated into several chartered fraternities, leaving under the control of the Weavers' Company only the branches of the trade dealing with broad silk textiles. Owing to Huguenot immigration, however, this single section of the weaving industry grew to enormous proportions, and the Company was unable to control it.

The Weavers made frequent appeals and petitions for protection to the King in Council and actually employed Daniel Defoe to conduct a periodical, called *The English Manufacturer*, advocating the use of English-made goods by the English people. To explain this resort to what we would now call a "press officer", it should be realised that the author of *Robinson Crusoe* was a very clever journalist and up to many of the "tricks" of his modern successors.

In the eighteenth century the operative weavers in Spitalfields became very different from their orderly and respectable Huguenot ancestors. On one occasion they demanded Parliamentary prohibition of the use of printed calicoes, and troops and train-bands sent to disperse them could not prevent them from tearing off printed calico garments from ladies they met in the streets.

During the eighteenth and early part of the nineteenth century the Weavers' Company gradually lost control of the trade and, retaining only its name and endowments, became little more than a benefit society for its members.

The Weavers' Company is rich in charters, but is now governed by a Charter of Queen Anne, which gives it a constitution unique amongst the City Guilds. The Company has no Master, but is governed by an Upper Bailiff, a Renter Bailiff, an Upper Warden, a Renter Warden, and a Court of Assistants.

The Weavers' Company was for centuries established in Basinghall Street. Its Hall, rebuilt after the Great Fire, was pulled down in the middle of the last century, and replaced by a block of commercial offices somewhat misleadingly styled "Weavers' Hall".

Since the middle of the last century the Weavers' Company has taken on a new lease of life. It has been in the forefront of the movement amongst the City Companies to be of service to the industries which they were incorporated to foster. Weavers are notoriously cheerful folk: Shakespeare, you may remember, wrote—

I would I were a weaver
I could sing all manner of songs.

FRAMEWORK KNITTERS

If the origin of the Guild of Weavers is lost in antiquity, that of the Framework Knitters is more or less known, and is sufficiently romantic. It seems that a Master of Arts of St. John's College, Cambridge, called Lee, fell in love with a country maiden, and was very disappointed to find that the young lady was more intent on knitting her hose than on entering wholeheartedly into the delights of courtship. The lover was extremely piqued that mere knitting-needles should prove superior to his own attraction, and set himself to devise a machine which would make hand-knitting unnecessary. He was evidently of an inventive turn of mind, and in due course evolved the first frame for mechanical knitting. Lee's descendants and their associates were successful in establishing framework knitting in London, Godalming, and Nottingham, and by the middle of the seventeenth century the industry was so well organised that Oliver Cromwell granted the craft a charter of incorporation.

In these luxurious days, when silk and nylon stockings are worn by every woman, high and low, it is hard to realise that there was a time when even royal legs were swathed in coarse cloth.

In the time of Queen Elizabeth I, hand-knitting was little practised and something of a novelty. There is, of course, a good story of Queen Elizabeth's first pair of silk stockings. These were presented to her in the presence of Lords Leicester and Burghley, by Mrs. Montague, who had recently acquired the art of hand-knitting. My Lord of Leicester flattered; Lord Burghley chided against such frippery. Finally Her Majesty retired, returned with the stockings on, and said—"Gentlemen, the silk stockings do fit me right well, and I like them much because they are pleasant, fine, and delicate; and henceforth I will wear no more cloth stockings."

The Stuart Charter gave the Guild of Framework Knitters executive powers extending throughout England and Wales, and all mayors, bailiffs, constables, etc. were ordered to assist the officers of the Company, or their sworn deputies, in carrying out supervision of the trade. Two or more of the governing body were empowered to go on search, and if they found bad work, to destroy it and fine the manufacturers.

By the middle of the eighteenth century, however, the Company came into conflict with the House of Commons, and certain of its regulations were regarded as vexatious and in restraint of trade. A lawsuit in 1809 sounded the death-knell—for a time—to the Company's influence, as it was declared that its Charter controlled only its members, and that non-members might engage in the industry without any supervision or interference from the guild or its officers.

The Company went downhill for some years. In 1821 it sold its Hall to the Corporation, and in 1861 had to sell its plate to repair its almshouses, which had been established early in the eighteenth century. Then came the turn of the tide. The Company wisely followed its craft to Leicester, and is again a great power in the trade.

THE WOOLMEN

The Woolsack is a permanent memorial of the importance which was attached to wool as the chief source of our national wealth in the Middle Ages. Queen Elizabeth I caused the seat of the Lord High Chancellor to be fashioned of a sack of wool, as a reminder of the pre-eminent position then occupied by wool in the commerce of the country.

In view of the value attached to wool it is not surprising to find that a guild was formed at an early date by the craftsmen dealing in this premier product. The Woolmen's Company had a Hall near old Wool Wharf. It was destroyed in the Great Fire, when all the Company's records perished with the notable exception of a book of ordinances approved in 1587 by the Lord Chancellor and two Judges. The Company has no Charter and acts by prescription.

THE MERCERS COMPANY

Carlyle said: "Society is founded upon cloth". Be that as it may, the senior Livery Company is the great and wealthy Mercers Company, which manages St. Paul's and Colet Court Schools. It is interesting to note that, of the other senior Companies which are concerned with cloth—the Drapers, Merchant Taylors, Haberdashers, and Clothworkers—all are concerned also with education on a big scale.

The word *mercier* originally meant a dealer in any kind of goods. The root of the word is the same, through the French word *mercier*, as that of "merchant", "mercantile", and "merchandise". Latterly, however, to be a mercer has meant to be a merchant in silks and wool cloths. To-day, I suspect that a "mercier" would deal in fabrics woven or knitted of man-made fibres too.

The Mercers have many distinguished benefactors, the most noted being Sir Richard Whittington and Sir Thomas Gresham, who founded the Royal Exchange and Gresham College. The Mercers' Hall is in Ironmonger Lane off Poultry, and the Drapers' Hall in Throgmorton Street.

THE DRAPERS COMPANY

At first the Drapers were general merchants dealing in foreign cloth and other articles. When the importation of foreign cloth was forbidden, they turned their attention to the export of home-grown wool. As the home cloth industry developed, they devoted themselves to the wholesale exploitation and exportation of homespun. They did not actually manufacture cloth, but they appear to have supervised its manufacture and to have carried on businesses, such as the making of liveries, which to-day would be regarded as the work of a tailor. As merchants they first appeared, and as merchants the most prosperous of them chiefly remained, while the less opulent of their craft turned to the retail trade and served their customers in their shops.

The Drapers were from their very beginning men of substance, but the statement by Ditchfield, that Henry Fitzalwyn, first Mayor of London, was a

Draper, is not regarded seriously by the Company's own learned historian. Before the end of the thirteenth century, when they became so truculent, we find Drapers as Mayors, Aldermen, Sheriffs, and even Members of Parliament. It is recorded that John de Lincoln, a Draper, lent money to Edward I for his French wars, and indeed there is no doubt that as early as the end of the thirteenth century the Drapers were moneylenders as well as merchants in cloth.

Their Charter from Edward III gave the Drapers complete control of their trade. The Dyers, Weavers, and Fullers were to keep to their proper crafts and in no way meddle with the making, buying, or selling of any manner of cloth or drapery on pain of forfeiture. No one who had cloth to sell could sell it except to a Draper unless to the Lords or Commons for their own use, and even then only in gross and not in retail. The Drapers acquired control of the sale of cloth at the great fairs, especially at Smithfield and Southwark, where they shared with the Taylors the right to search all cloth exposed for sale, and to mark it accordingly to its width and length, using their ell or standard.

The wealth and importance of the Drapers in Tudor days are evidenced by the fact that they were asked by Henry VIII to assist in fitting out a ship for the exploration of Newfoundland. The reluctance with which the Company furnished Sebastian Cabot with his vessel was in sharp contrast to the eagerness with which the Drapers threw themselves and their wealth into all the schemes for exploration and trade which sprang into existence under the encouragement of Queen Elizabeth I.

THE MERCHANT TAYLORS COMPANY

The Merchant Taylors were organised as a religious fraternity of St. John the Baptist as early as the thirteenth century. With the other greater guilds the Fellowship of St. John received a charter from Edward III, and in subsequent charters the Brotherhood was granted great powers over its trade. This supervision was largely centred on the sale of cloth at fairs, shared with the Drapers, and right up till 1854 the Company's representative used to attend Bartholomew Fair, at Smithfield, and tested the measures used for selling cloth by means of their silver cloth yard, which was the official standard of measurement. Alas! the Taylors' yard is no longer used, but it is preserved at their Hall as an interesting memento of the Company's former power over the cloth trade.

The Taylors did not rise to such wealth and importance in the Middle Ages by making garments or even by selling fabrics for making them. They were closely connected with the trade of the soldier, as their primary occupation was the making of garments to wear under, and ease the pressure of, suits of armour. They were not merely tailors in the modern sense but linen armourers.

In addition to making, so to speak, underclothing for the comfort of the knight or man-at-arms, they also manufactured surcoats, caparisons, and accoutrements. More, they were the first makers of tents for military and ceremonial purposes, a

fact which is proudly recorded in their arms. One might expect to see scissors or needles depicted on the escutcheon of the tailor's craft; but no! the shield bears three tents and the lion of England!

No doubt the Taylors' early trade in tents and military equipment brought them into close contact with the warlike Plantagenets and their successors, as the Linen Armourers must have been an important section of the munition workers in our earlier wars. Even in peacetime their services were important, as their sovereigns had to rely on the tailors to provide them with robes of State, and indeed everything worn by noble and knightly warriors and their retainers, except the actual metal work.

THE CLOTHWORKERS COMPANY

Trade is the soul of the kingdom, so the greatest branch of it lies in the Clothworkers' hands; and though our naval commerce brings us in both the "or" and the "argent" and indeed, the whole wealth of the world, yet when thoroughly examined it will be found 'tis your cloth sends out to fetch them.

So wrote Elkanah Settle of the great Company of Clothworkers.

The craft is very ancient, as we find a guild of Clothworkers amongst the adulterine guilds in 1180, and in the great battle between the Goldsmiths and the Taylors in 1267 the Clothworkers joined in the fray.

Although we find these early references to Clothworkers, the present Company did not come into being as a single Fraternity. It arose through a union of two associations, called *Fullers* and *Shearmen*, who were originally subsidiary to the ancient Guild of Weavers. The Fullers were a craft whose business it was to *full*, i.e. scour, cleanse, or thicken cloth. They employed a plant called *teasel*, or *matfellow*, in the process, and it is interesting to recall that they obtained this plant from the fields of Whitechapel. The Shearmen were workers whose business it was to finish cloth and shear or level the nap. They had a Hall of their own in Mincing Lane on part of the present site of Clothworkers' Hall. The two crafts were amalgamated by Henry VIII and granted a Charter as the Guild or Fraternity of the Assumption of the Blessed Virgin Mary of the Art or Mistery of Clothworkers in the City of London.

Pepys was a Liveryman of the Company and Master in 1677. He commemorated his year of office by presenting a beautiful silver cup, a rose-water dish, and a ewer, which are amongst the most cherished possessions of the Guild. In his immortal diary Pepys records the burning of old Clothworkers' Hall. "But strange it is", he writes, "to see Clothworkers' Hall, on fire these three days and nights, it having its cellars full of oyle".

The Clothworkers have done much for the wool industry of Yorkshire and have spent vast sums—as long ago as 1931 it was a quarter of a million pounds—on Leeds University and the old Dyeing and Textile Department of the Yorkshire College before the formation of the University.

THE DYERS COMPANY

Unlike so many other industries, the craft of the Dyer was truly indigenous, but perhaps the ingenious coloration of fabrics and of leather was little more than an evolution of the ancient British custom of staining the body with woad and other pigments! Simple vegetable preparations were used in Saxon times to dye their simple homespun. Records point to the existence of the Guild of Dyers in 1131 (nearly as old as the Weavers), and it is certain that as early as the fourteenth century the industry was so far advanced that its craftsmen could produce almost any variety and shade of colour. Edward IV incorporated the Guild in 1472. With the prevailing partiality for bright and showy garments, the medieval Dyer found his occupation particularly profitable, and he waxed in wealth and power.

Sir Frank Warner tells us that in France the art of dyeing was divided into two classes, grand and lesser dyers. The great dyes had to stand the test of "twelve days' exposure to the summer sun and the damp air of night". To-day we use a fading lamp!

The colouring pigments used by the Guild of Great Dyers in France were, with the exception of the crimson of cochineal, extracted from vegetable substances—woad furnished the blue tints, welds the yellows, and the madder root the reds. Welds dyed upon woad produced greens, welds upon cochineal orange, cochineal upon woad purple, while cochineal upon a tin mordant gave a brilliant scarlet.

In the reign of Edward VI an Act of Parliament was passed limiting the variety of colours the dyers might use to scarlet, red, crimson, murrey, pink, brown, blue, black, green, sadnew colour, azure, watchitt, sheep's colour, motley, and iron grey. It is now impossible to assign the exact colours to some of these quaint names. They all no doubt resulted from the manipulation of the few natural dyestuffs just mentioned.

Indigo, introduced into France from India as a substitute for woad, was long resisted, as was the introduction of logwood in Elizabeth's time. This dye was used clandestinely for 100 years until the prohibition of the twenty-third year of Elizabeth I was repealed by statute in the fourteenth year of Charles II.

In 1530, Stow records, the Dyers were in the list of great Companies, but since that date the Clothworkers have taken the Dyers' place.

An Act of Parliament passed in the reign of George I made all persons engaged in the dyeing of wool goods within the City of London subject to inspection by the Company of Dyers. The Company was empowered to appoint "searchers", who were empowered to enter shops and "work-houses" to ascertain whether goods were properly dyed. Persons opposing the Dyers' searchers were fined £10, and all forfeitures went half to the Dyers and half to the informers. These powers were actually increased in 1783, but have long since fallen into disuse.

For many years the Dyers' Company took little interest in the great industry whose name it bears,

and it is a matter of history that the British dyes were largely ousted by foreign competitors, who exploited the great discoveries of our own Sir William Perkin, in the utilisation of coal tar. During and since the first World War, however, the great Fraternity has once more been interesting itself in the production of dyes in this country. The Guild no longer seeks to control the craft by means of its Charter powers, but endeavours, through the encouragement of research and in other ways, to restore its position of supremacy to the truly British industry of dyeing.

MEDIEVAL CRAFTSMEN

It is obviously impossible in one short hour to trace the history of weaving and printing in London and the Home Counties for some eight hundred years, and with this brief sketch we must leave the history of the ancient textile Livery Companies of London as such. But let me quote just a few references taken somewhat at random to throw the spotlight on our textile predecessors in the thirteenth and fourteenth centuries. We cannot, however, avoid mentioning again some of the guild craftsmen, who were in such complete control of their trades.

In 1298 it was complained that certain Fullers had sent cloths, entrusted to them to be fulled, to the mills at Stratford, when they ought to have been fulled "by the feet of men of the craft or their servants in their houses within the city". A committee of Dyers, Tailors, Burellers, Weavers, and Fullers was accordingly appointed to make provision for the better regulation of the Fullers' craft.

The origin of the word *bureller* is obscure. It is likely that the Burellers gained their name from *burel*, the coarse cloth the London Weavers are mentioned as making in 1218 and 1225, and which may reasonably be identified with the cloth of Candelwick Street woven by men of the same guild at the end of the century. At a very early period, "in time whereof memory does not run", according to a record of 1300, it had been necessary to regulate the relations of the Weavers and the Burellers. This suggests that the Burellers were gaining some direction over the Weavers in the early thirteenth century at the latest. In the end they became a sort of cloth converters, and as the number of cloths increased, the name as such ceased to exist and the Burellers became Clothworkers and Drapers.

A good deal of disputing went on between the Weavers and Burellers, and there were even sympathetic strikes, which the latter could not tolerate. This weapon was known in the thirteenth century and used several times in the fourteenth. Moreover, all customs which hindered rapid production were condemned—

And whereas it was forbidden in their craft that a cloth of forty ells should be woven in less than four days, it is provided that each may make it in as short a time as he can, provided it be well and lawfully wrought. And whereas it was forbidden in the craft that any weaver should work between the Tiphany and Candlemas [i.e. between January 6th and February 2nd], it is provided that each person in that season may boldly do so, just as well as at other times of the year, without challenge and without hindrance; provided that he work well and lawfully and that he do not work by night.

The interests of Weavers and Burellers were directly opposed: the Burellers wanted to stimulate production, the Weavers to raise prices by restricting supplies. Nothing else can account for the fixing of a minimum time for weaving a cloth, nor for the long cessation of work in January.

In spite of the desire to accelerate output, night work was still forbidden. The prohibition was general among the crafts. It was felt that night work tended to lack finish because of the weak artificial light and the unlikelihood of scrutiny; it was a disturbance to neighbours, and was unhealthy, as leading to overlong hours and undue competition.

POLICY OF EDWARD III

The policy of Edward III (1327–1377) towards trade and industry was definite. He desired to increase the volume of trade and to obtain a plentiful supply of cheap food. He wished to develop the cloth trade as an industry bearing promise of lucrative returns. Englishmen would be independent of the foreign market, which was disturbed in time of war, if the wool was manufactured at home instead of being exported. Edward was free from insular objection to the foreigner. Hence he gave facilities to alien traders, thus engaging himself in a long duel with his native merchants, particularly those of London. At the end of the reign the narrow policy of the citizens won, though the struggle was continued under his successors. He invited skilled Flemish weavers to England to teach their art, to the anger of the native craftsmen he designed to profit.

Edward III did not originate the plan of introducing alien weavers to England. Henry III had granted that—

All workers of woollen cloths, male and female, as well of Flanders as of other lands, may safely come into our realm there to make cloths . . . upon the understanding that those who shall so come and make such cloths shall be quit of toll and tallage, and of payment of other customs for their work until the end of five years.

In the Ordinance of the Staple, Edward II made a similar promise.

In a further Ordinance of the Staple of 1st May 1327, Edward III repeated his father's decree that the commons of England must wear cloth made in England, Ireland, or Wales, and continued the promise of "suitable franchises to the fullers, weavers, dyers and other clothworkers". In 1331 he issued letters of protection to John Kemp of Flanders, weaver of woollen cloths, on the understanding that he came to England with his men, servants, and apprentices, "to exercise his mistery and to instruct and inform those who wished to learn from him". The King deliberately aimed at spreading technical skill. In the same letter he offered protection to any other weavers, dyers, and fullers from overseas willing to dwell in England for the same cause.

In 1332 he ordered it to be proclaimed in London "that, in view of the decay of the art of weaving, no person for two years from Christmas next, shall use or wear cloth not made in the realm, if he have not 100 marks of land or rent".

Again, it is recorded that in a royal writ, dated 1st November 1432, the Mayor of London and his colleagues stated that—

there had always existed in the city and suburbs, three separate and distinct misteries of native clothworkers, viz: native weavers of woollen cloth for Tapestry, native weavers of woollen cloth for Drapery, and native weavers of woollen cloth for Napery, and that of these three only the weavers for Drapery have always had a gild of their own.

Stow differentiates only two kinds of weavers, and speaks of weavers of Napery existing in the time of Edward III. He says that "there were then in this city weavers of diverse sorts, to wit of Drapery or Taperie, and Naperie". It may be that the mystery of linen weavers developed from the weavers of Napery, though these are described as workers in wool in the Letter Books. But linen weaving was practised in London before this reign: witness the writ of 30th August 1315, addressed by Edward II to the Mayor and Sheriffs of London to make proclamation that no merchant sell canvas, linen cloth (*lineam telam*), napery, or like cloth without checking by the Aulnager. No doubt linen weaving, like woollen weaving, developed under the care of Edward III. The country needed its supplies of linen yarn in his reign, for in 1363, when an order was sent to the ports and other towns forbidding the export of various articles, linen as well as woollen yarn was among the list of prohibited goods.

THE TRADE UNDER ELIZABETH I

However interesting these old records may be, and however surprised we are to find the activities of masters and men strangely similar at times to their actions of to-day, we can add only one final word. The Weavers of London were amongst the fourteen small crafts who were concerned in 1556 in the order of the Common Council of the City fixing the number of apprentices for each householder. To-day a block-printer cannot increase the number of his apprentices without the approval of the relevant trade union.

At the end of the sixteenth century we find the Weavers complaining bitterly about the way that immigrant weavers flouted the rules and regulations of the craft, one complaint being that they avoided observance of them by going "into the country five or six miles from the City out of our liberties and there maliciously keep and do what they will".

In the reign of Elizabeth I the trades and industries of England experienced a time of steady growth. In the same way that seafaring, encouraged as it was by the Queen, led to Great Britain's ultimate supremacy at sea, the wool trade, then the most important industry in the country, took on proportions which in the succeeding centuries assured its ascendancy over the textile trades of the Continent. The 60,000 pieces of woollen cloth that were annually exported by the Company of Merchant Adventurers in the late fifteenth century doubled in less than fifty years. The greater part of English cloth manufacture was exported undyed as it came from the loom until far into the seventeenth century, and was processed by the dyers

and finishers of Flanders and Brabant. Since Edward III's time the English kings had hoped to emancipate the native cloth industry from the foreign finishing processes, but were opposed by the Merchant Adventurers and staple merchants, who had great difficulty in selling cloth dyed and finished in England. Henry VII, the first Tudor king, in 1487 forbade the export of any stuff which was not fulled, teazled, or shorn. Only certain cheap-quality cloths were to be shipped abroad. In 1565 Queen Elizabeth issued a decree which was to reconcile the interests of the merchant companies with those of the members of the finishing trades. By its terms the counties of Kent and Suffolk were ordered to cease the export of white and unfinished cloth, as the London shearmen and dyers were dependent, in the first instance, on the manufacture from these districts. The merchants, on the other hand, were bound to sell at least one piece of finished cloth with every nine pieces of loom cloth, a regulation which was somewhat attenuated by licences and special privileges granted to the Merchant Adventurers. In spite of this, they complained in a petition addressed to Lord Burghley in 1593 that they were unable to sell their finished cloths except below cost price, and asked for the abolition of export restrictions. But the decree of 1565 remained in force until 1707, after which year half-finished goods were charged with export dues, while finished stuffs could be sent abroad duty-free.

That the wool-weaving industry of London was freed from the foreign finisher—however long the struggle lasted—is obvious to-day, for *London-shrunk* is the hall-mark by which finished wool cloth is judged and bought by buyers all over the world. The degree of shrinking implied by the term is not now confined to London, but it is a term of commercial integrity which obviously springs from the pride of craftsmanship implicit for the last 800 years in the ordinances of the great craft guilds of the City of London, to which I have devoted so much time.

TAPESTRY

Inspired by Henry IV of France, James I of England set up tapestry workshops at Mortlake in 1620. This village, mentioned in the Domesday Book, is famous for two other events—the University boat race finishes at Mortlake; and I was born there!

Most Mortlake tapestries are English more by courtesy than in fact, because the weavers and the cartoons were imported from Flanders, or the cartoons were painted by Flemings. The one notable exception is the *Battle of Solby* series in Hampton Court Palace.

The Victoria and Albert Museum have kindly lent me a photograph of a typical piece of Mortlake tapestry.

Again, in the eighteenth century Flemish weavers in England (notably John Vanderbank) produced in Soho (somewhere between Lincoln's Inn Fields and Drury Lane) picturesque and distinctive grotesques in the chinoiserie taste. I have also a photograph of this type of tapestry

and a sample of a hand-block-printed linen, the design of which is said to have been taken from a piece of Soho tapestry, although I can see little Chinese influence in it.

SILK

So far my references to fibres have been almost exclusively to wool and linen. I must now say something about silk, which looms so large in the textile history of London.

It may first be noted that the versatile scientist Robert Hooke, Curator of Experiments to the Royal Society and Professor of Geometry in Gresham College (administered, by the way, by the great Mercers Company) published his *Micrographia* in 1664, in which he visualised the possibility of making an artificial fibre by a process similar to the spinning of the silk worm. Two centuries were to elapse, however, before this possibility became even a probability, and another half century before it became a certainty.

We find silk being used in London in the fifteenth and sixteenth centuries, but largely for embroidery for use with gold and silver thread, for the weaving of ribbons, trimmings, and trappings generally, and even for knitting stockings.

It is, however, to the Huguenot refugees who flocked to England in 1685 that the glorious chapter of the Spitalfields broad-silk industry is owed. Perhaps I may be permitted to quote from a lecture given by my colleague Alec Hunter on the history of my firm, which is so wrapped up in the weaving history of Spitalfields. He says—

The beginning of my story is the settlement of the weavers by the Bishops' Gate in East London. During the 16th and 17th centuries, the craft of silk weaving spread from Italy to France and the Netherlands where it developed into great and prosperous industries. From time to time, during these centuries, refugees from the Netherlands came to England and helped to develop the silk industry of which Spitalfields was a centre. But the largest and most important immigration and one which established silk as a great industry in the country was in 1685 and the years following. In that year the policy of religious toleration practised in France was suddenly reversed and an organised and remorseless persecution of Protestants started. The weavers suffered greatly. No one was allowed to leave France and the penalties for attempting to do so were condemnation to the galleys or prison for life. Nevertheless, thousands fled. Among those whose names are recorded I would mention that of Augustine Courtault and his infant son.

To the lasting credit and certainly to the benefit of this country, these Huguenot refugees were welcomed. Funds were raised for them and Parliament voted £200,000 for their relief. In one year 15,000 refugees had settled in London alone and, of these, those who were weavers, settled in the weaving district of Spitalfields outside Bishopsgate. They were welcomed by the weavers already there, many of whom were dissenters, including a large number of Quakers, who had themselves suffered comparatively mild forms of persecution at the hand of authority.

The Settlement prospered and soon velvets, brocades and damasks and other fine silks were being produced and the monopoly of France in these things was broken. They were indeed "profitable strangers". Houses were built and contemporary accounts describe it as a pleasant district, inhabited by pleasant people; keen and ingenious at their work and delighting in their gardens and singing birds. It has been said that the love of gardening and flowers that became so characteristic of the English was in part taught them by these refugees. The Spital-

fields weavers founded the first gardening societies in England. They also founded the first Friendly Society in 1703.

[Here Sir Ernest showed two original Spitalfields designs from the Victoria and Albert Museum—one the original paper sketch, and the other a woven fragment.]

Towards the end of the 18th century, much of the silk industry migrated from London. One of the causes of the migration was said to be the Spitalfields Act of 1773 which fixed the weavers' wages in the London area; at any rate, many firms found it profitable to move their works into such counties as Essex and Suffolk where the old wool trade was declining and where many workers were available. This movement continued and no doubt was encouraged by the development of machinery for throwing and the increasing use of water mills for power. It was at this time that the silk industry reached Braintree.

Less prosperous times came to Spitalfields towards the close of the 18th century, and the early 19th century saw a fall in the status of the operative weaver and a terrible period of poverty. The original community of master weavers gave place to the successful master and the operative who worked for him. Classes among the weavers arose with a middle class which included these master weavers, as well as dyers, warpers and others. The master weaver remained a fine craftsman and, for those who are interested, I would recommend Sir Frank Warner's essay "A Typical Silk Master" which is a beautiful and even a lyrical piece of writing describing a master weaver as Sir Frank himself may just have remembered him. He notes with interest that the grand-daughter accompanied her father's violin, she being the first of the family to be taught the piano, and also the first daughter not to be taught some branch of weaving.

One reason for the change in structure of the community was probably the development of the jacquard. In the days of the drawloom, one family would weave the same design for many years, or even a lifetime. With the advent of the jacquard, frequent changes of design were required and the harness maker and jacquard engineer, with the designer, joined the ranks of the new middle class. It was into this trade of harness maker and jacquard engineer that Benjamin Warner, the founder of the present firm, was born.

The Warner family were at work in Spitalfields at the end of the 17th century. It is recorded that William Warner was already a scarlet dyer of Spitalfields before the big influx of Huguenots in 1685. He died in June 1712. His son and grandson carried on the business and their descendants remained at work connected with the industry either in Old Ford or Bethnal Green and, in the year 1828, Benjamin Warner was born. His father died when the young Benjamin was only 11 years of age. The child was taken from school and helped his mother carry on the business of harness maker and jacquard machinist in Punderson Place, Bethnal Green Road. He attended evening classes at the Spitalfields School of Design, an early government effort to promote design in industry and, later, becoming proficient in manuscript, he helped out his income by working at night for a firm of law stationers. The interest and knowledge of design obtained at the Spitalfields school and the discipline of fine manuscript writing stood him in good stead in later years.

Benjamin Warner took his first step in the new course he was to follow when he purchased the business of M. Bernier, a designer who, after practising in Spitalfields, decided to return to his native Lyons.

In 1870, Benjamin started the manufacture of furnishing silks. With him were two partners, and his new business soon prospered and markets for the fine fabrics he produced were found on the Continent and in America as well as at home. The excellence of his figured silk fabrics with their well chosen designs soon won a great reputation. In 1879, he turned his attention to the production of figured velvets and succeeded in producing the equal of those woven in Lyons.

In 1891 Benjamin's sons, Alfred and Frank, came into the business and the title then became Warner & Sons.

The first had begun at Old Ford. Most of the weaving was done in the houses of the weavers but it was desired to do more in the factory and, for this purpose, a new brick factory was built in Hollybush Gardens.

In the 1890's the revival of fine silk fabrics was greatly encouraged by the enthusiasm of the Duchess of Teck and her daughter, Princess May, later to become Queen Mary. Among their many activities to help the industry and to foster an appreciation of British silks was a tour of inspection in 1893 of some of the leading silk centres. The first visit was to Warners' new factory in Hollybush Gardens and this was a red-letter day in the history of the firm. It was here that the Princess's wedding dress was woven of silk and silver thread with an exquisitely drawn design. This was the beginning of a succession of royal orders with which Warners' have been honoured up to the present day.

Mr. Hunter refers to the drift into Essex and Suffolk after 1773, but even before then several small silk-throwing mills were established in Essex, one of which was at Sewardstone, near Waltham Abbey, established about 1720. A century later it is described as a "small silk mill in the occupation of Messrs. Carr & Dobson, Foster Lane, Cheapside". A hundred years ago this mill was used for dyeing and scouring. It ceased to exist about 1885.

The mill at Pebmarsh, now pulled down, is interesting as having been started in 1798 by George Courtauld, whose great-grandfather was the refugee aristocrat from France mentioned by Mr. Hunter. It is interesting to note that this Huguenot fugitive was not in the silk trade. His son and grandson were gold- and silver-smiths. It was great-grandson George who began the silk mill. George subsequently moved to Braintree, in 1810, and so began Braintree's contact with silk. It is, however, to George's son Samuel that credit is due for laying the foundations of the firm as we know it to-day. We cannot afford more than a passing reference to the grit and determination of the directors of that great enterprise, who, persisting in the development of artificial silk, laid the foundations of the rayon and synthetic fibres industry we know to-day. It is also worth recording that Courtaulds took viscose rayon to the United States and had a controlling interest in the American Viscose Corporation until they were forced to sell out for dollars early in the last war. They have recently set up a new subsidiary in the U.S.A.

Saffron Walden, Bocking, Halstead, Coggeshall, even East Ham and Stratford, all saw silk throwing or weaving in the early part of the last century, and it was the long-established mills of Daniel Walters & Sons at Braintree—exhibitors at the Great Exhibition of 1851 and at others—which Warners' took over in 1895 when they too moved out of Spitalfields. In 1841 the silk industry in Essex gave employment to 1582 persons, and by 1861 over 3000 were so employed.

Sir Frank Warner in his book says that in the year 1853 the writer of the *Survey of London's Trade* gives 14,000 as the number of hand-loom weavers in London, and that by 1914 there were but forty-six workshops still occupied by weavers

in Spitalfields, mostly in the Cranbrook Street and Alma Road neighbourhood in the extreme east of Bethnal Green. By 1931 only a scattered group of eleven remained. Even this number dwindled further in the decade before the war, and I know of no weaver practising his craft in the East End of London to-day, exactly a century since the 14,000 flourished. Fleur-de-Lys Street, Blossom Street, Fournier Street, Flower Street, and Rose Alley, if they have survived the bombing, have only their memories to cherish.

PRINTING

Apart from weaving, there is, of course, another very large branch of textiles, the decorative effect of which is obtained by printing. The first textile-printing works in Great Britain are said to have been begun by a French refugee towards the end of the seventeenth century—about 1690, only five years after the revocation of the Edict of Nantes—on the banks of the Thames near Richmond, and soon after, according to one record, a more considerable factory was established at Bromley Hall in Essex. About 1760 a printworks was also established at Old Ford, east of the City. I cannot find much about this establishment, but the Victoria and Albert Museum have lent me two fine original specimens of the printing of this Old Ford works.

Spitalfields, Old Ford, Essex, are all north of the Thames. However, there are—or were—many clear streams flowing down from the chalk hills of the North Downs in Surrey and Kent to the River Thames. On these streams there became established paper mills and textile-printing works. There are three rivers worthy of special mention—the Darent at Dartford, the Cray at Crayford, which runs into the Darent before it crosses Dartford Marshes, and the Wandle at Merton.

On the Darent at Dartford a textile hand-block printworks became established during the last century, part of which was in what was at one time the stables of the old Bull Inn at Dartford, one of the coaching stages made famous by Dickens. The land belonged to an ancient charity called "The Corporation of Wardens of the Parish of St. Saviour in Southwark", which owned also the Borough vegetable and potato market.

The Dartford Printworks were let to Newman, Smith & Newman, who did some fine work there, printing linens and chintzes, bedspreads and flags. Unfortunately they felt the depression after the first world war, and these works came into the possession of my firm. During the twelve years before the outbreak of the last war, Warners' spent a lot of money on these works, building a new river wall and laying down tables for the new screen printing process. The works were, however, closed on the outbreak of war, and the blocks and screens transferred to other printers. The premises are now used for storage. They were not up-to-date enough to be re-opened after the war.

I have here a few specimens of Dartford prints. The first is a scarf printed from an engraved plate in 1904 to commemorate St. Amant winning the Derby and the 2000 Guineas. This scarf was given

to me by the old foreman-printer, Mr. Gibling, who originally printed it. The second is a length of printed linen lent me by Mr. Dines; the third is a hand-block print containing 182 blocks for the one print of the design, which is 54 in. long by 50 in. wide. The fourth is an early example of screen printing which was developed at that works. The next is a good example of fine work in a furnishing chintz design, and the sixth is a sample of the screen-printed linen produced specially for the Committee rooms of the House of Commons before the war, and used again on a dyed linen for the rebuilt rooms two years ago.

There are two works at Crayford on the Cray. The first is the Swaisland Fabric Printing Company, which has been there since about 1700, when calico from India was bleached in the surrounding fields. In 1702 whittsters were buried in Crayford Churchyard. Since then, there has been no break in the continuity of the industry in the village. Charles Swaisland, who flourished in the early part of the last century, gained a great reputation and did very creditable work, as the pattern books left by him record. He covered a wide field of work, printing by wood blocks, plate, and machinery on silk, wool, cotton, and linen. Shawls in wonderful Paisley patterns, flannels for the West Coast of Africa inspired by Landseer's paintings of animals, and blazer flannels for Universities and clubs. When Swaisland died in 1865 the Swaisland Printing Co. Ltd. was formed to carry on the works, but in 1893 it went into liquidation, and Messrs. G. P. & J. Baker took over this ancient, yet up-to-date printworks. This firm now confines its work mostly to decorative fabrics for furnishing, and I have several old and current samples to illustrate this fine old firm's work. Its grand old man, Mr. G. P. Baker, died only a matter of months ago, in his nineties.

The other firm at Crayford is David Evans & Co. Ltd., whose Managing Director, Mr. Roy Hind, has given me some interesting notes about his works and lent me some interesting samples of old and current prints.

There is a record that calico printing was carried on at these works as long ago as 1760, and whether Baker's works or Evans' works were first is not for me to say. This date roughly corresponds with the establishment of the works at Jouy near Paris which Oberkampf made famous.

In 1829 a Mr. David Evans of Wood Street, London, took over these Crayford works, and I have a paper print of a design for a table cover produced by him there in 1852, i.e. 101 years ago. To-day these works produce some of the finest hand-block and screen prints, the fastest dyes known being used, and the whole plant has been brought up to date. Here are some examples of work done there 100 years ago, and some scarves produced there to-day.

[*Samples displayed.*]

The last printworks to which I wish to refer is that of Messrs. Liberty Ltd. at Merton Abbey in Surrey on the Wandle; Merton Abbey has a famous history.

It was about 1740 when a Mr. Halfhide set up a calico print works at Merton Abbey, within what had formerly been the priory grounds. The river Wandle had been canalised and was some 15 ft. above the surrounding ground, and therefore lent itself admirably to supply water to the ditches which were cut across the meadows, and from which water was splashed on to the calico spread out on the grass in the sun to bleach.

From that date until about 1840 there is a gap in the history of the works. But at about that time a Mr. Littler or a Mr. Laurence brought some printers over from Ireland and joined what was probably a small community of printers, each of whom had his own print shop but who shared communal dyeing and steaming arrangements. These arrangements probably continued to the end of the century or thereabouts, and one of the print shops is still known as "Coles' Shop", it being the one in which Mr. Coles' set of printers worked.

In the 1890s and early 1900s, Liberty & Co. were taking all the production from Mr. Littler's printworks, and eventually bought the printworks and some thirty acres of land. At that time there were two water wheels in working order, one of which is still used in the processing of their fabrics. The other one appears to have been used for grinding colours, as the stones are still there.

There was a disastrous fire in the 1870s, which burned many of the old blocks, but nevertheless many of the designs for which Liberty's have become renowned, and which are still used, are printed with blocks at least a century old. Some of the finest examples of stippled work in their possession probably date from 1790 or earlier.

Since the war Liberty's have re-equipped their screen printing shop, and I am able to show you some examples of screen printing which they have done, and which I think you will agree are remarkable for their fineness of outline and accuracy of fitting.

It is appropriate to refer here to another works on the other side of the Wandle and a short distance downstream. In 1871 William Morris, as part of his campaign to resuscitate handwork in order to combat the human ills resulting from machine production, established tapestry looms which in 1877 were moved to Merton. Cartoons were supplied by Morris himself in designs of plant forms in his careful style, while figure pieces were supplied in the pre-Raphaelite manner by Edward Burne-Jones. Several of these tapestries, with their clear but rather heavy colours, have recently been on view at the Victoria and Albert Museum in the exhibition illustrating the work of Victorian and Edwardian designers. Mr. P. Floud has very kindly lent me several original examples of Morris's work.

WHOLESALESAERS

Wholesaling in England is as old as merchanting, and in my sketch of the great Livery Companies of the City of London I have already referred, if indirectly, to the wholesaling activities of the

Drapers and Merchant Taylors. Another great Company was that of the Merchant Adventurers, who traded over the seven seas from the Port of London. The wholesaling of textiles was a major occupation of many of the citizens of London during many centuries before the nineteenth, and wholesaling did not owe its origin to the Industrial Revolution, as is thought by some.

In the Middle Ages much of the selling of cloth and clothes was done at trade fairs, to which merchants took their goods, usually by pack-horse. The decline of the trade fairs appears to have begun in the middle part of the eighteenth century, which coincided with the making of roads and canals. With the making of the roads came what was known as the "fly-waggon", which was a great lumbering waggon drawn by some half-a-dozen horses, whilst the building of canals saw the inception of the canal boats. These two new methods of transport displaced the pack-horse, and towards the end of the eighteenth century and the beginning of the nineteenth, carriers commenced regular deliveries of goods to and from most of the principal towns. From about the middle to the end of the eighteenth century the method of selling adopted by the wholesalers appears to have been through the medium of the well known City Inns. It seems that it was a habit of the wholesale merchants to meet their customers at the taverns, where they conducted their business transactions under leisurely and, no doubt, hospitable conditions.

With the introduction of the warehouse system at the beginning of the nineteenth century, we find the wholesaler again adopting different methods of selling. Previously he had sought out his customers, but now that he had established a warehouse he naturally endeavoured to get the customers to the warehouse to see his goods. Some of the methods then adopted seem strange in the light of to-day's highly organised method of selling. According to Swindells, in his book entitled *Manchester Men and Manchester Streets*, in the early days of the warehouse system "hookers-in" were employed.

Country drapers coming to the towns to purchase goods had, of course, to travel by stage coach, and put up at one of the inns. The hookers-in haunted the coaching houses and inns in their search for information as to new arrivals. Armed with the necessary particulars, the hooker-in would call up the visitor, and endeavour to persuade him to allow himself to be escorted to his client's warehouse.

The merchants of those days adopted another means of securing the attendance of buyers at their warehouses. As soon as it was known that a probable customer had arrived in a town, which could always be ascertained by a reference to the waybills of the coaches recently arrived, a clerk was immediately dispatched to interview the visitor. It is on record that one gentleman who had arrived overnight from London was honoured one morning before breakfast by no fewer than forty such callers. Needless to say, the custom rapidly developed into a nuisance, and many were the indignant protests made by the victims of it.

As the means of travelling multiplied and became cheaper, firms began sending out travellers to call upon customers, carrying an array of samples that would have been impossible under the former conditions. The improvement and cheapening of the rates of postage and the introduction of the telegraph led to still further changes, and thus it was that the hookers-in and canvassing clerks disappeared.

So far as the history of the nineteenth century is concerned, it will be sufficient to say that the Industrial Revolution at the beginning of that century resulted in the processes of manufacture being altered out of all recognition, bringing a volume of output of manufactured goods hitherto undreamed of. In such circumstances, it was only natural that the wholesale warehouses should develop rapidly when masses of goods were being produced, so that it was necessary to have some system which would not only provide storage accommodation but also devise means of distribution of the finished products both at home and overseas. Thus it was that the warehouse system came into being in a form somewhat similar to that which we know to-day, for it was into these wholesale warehouses that the output of the factories found its way.

It is interesting here to record that many of the warehouses that came into being at the beginning of the nineteenth century still maintain a leading position in the wholesale distributive trade in this, the middle of the twentieth century. It would be invidious to mention them by name, but anyone connected with the textile trade will know that they are household names in wholesale distribution. There are a large number of such firms who have been in existence for well over a century, whilst there are many who have traded continuously for 150 years and upwards.

Let me now quote one or two extracts from *The Drapers' Record—Textile London*, describing the City of sixty or seventy years ago—

As for textile trade in Aldersgate Street, in 1794 there was none. The street possessed one glover, one linen draper, one mercer, one warehouseman, and one weaver. But to-day Manchester Avenue rises up—a modern addition to Aldersgate Street, as is the "Manchester" Hotel beyond it; both places serve to remind the reader of the vast and rapid growth of the great city of Manchester, sometimes called Cottonopolis. Its emissaries swarm over textile London day by day, and their choice of a temporary home is Aldersgate Street. [Warners' first London warehouse was in Aldersgate Street.]

Now let the reader walk up Gresham Street, from the west, beginning at the corner of Goldsmiths' Hall, and sundry things shall be pointed out to him. There is that solid-looking warehouse on the left next to Haberdashers' Hall. It is the house of Thomas Tapling & Co., famous for carpets, curtains, tapestries and all down-trodden things.

Milk Street is now an interesting thoroughfare only to the man of business. Linen and other manufacturers, or their representatives, hurry hither and thither between its dingy walls. They would smile at being told that seventeen textile traders in all inhabited the street one hundred years ago; but it was so. There was one glover, one laceman, two linen drapers, one mercer, one ribbon manufacturer, and eleven warehousemen.

In Wood Street, if anywhere, one would look for old names of those who built up the textile industry. Yet

there were but few textile trades established there a century ago. Here is a summary: of hat manufacturers there were two, linen drapers two, ribbon manufacturers seven, warehousemen six, weavers six, or a total of twenty-three. This was A.D. 1794. But—happy omen for the future of the thoroughfare—No. 1 was the warehouse of a ribbon weaver. To-day there are nearly 170 textile firms and manufacturers' agents in Wood Street, representing mills, manufactories, and warehouses with a gross capital of some millions of pounds sterling, and finding employment for many thousands of persons of all grades. But this tremendous increase in the second industry in the world began when the "toot-toot" of the coach gave way before the scream of the locomotive. Free trade blessed the increase, a cheaper postage fostered it, a more general education of the people nourished it, and better laws strengthened it.

And now let us walk down Wood Street as we find it to-day, noting anything which strikes us as we push our way along its narrow flags. There is the dark entrance to Mitre Court on the right—'tis a busy passage. A little farther down, on the same side, is the great hosiery house of the Morleys, a firm which gave a philanthropist and a statesman to the country in the person of the late Mr. Samuel Morley, one of whose sons has become Her Majesty's Postmaster-General.

How London has changed since then! The great textile centres round Wood Street and Fore Street, St. Paul's Churchyard and Paternoster Square, suffered such damage in the great fire raids on London in 1940 and 1941 that much of the wholesale trade that used to flourish in these centres has moved to the West End of London, and many of the general textile wholesalers are to be found north of Oxford Street nearer their brethren the woollen merchants, still faithful to the Golden Square area to the south of that street. Those City wholesalers who suffered little or no damage in the war have remained faithful to the City. Messrs. Morley's have returned, and if their great chief

Lord Hollenden had had the enlightened support of the planners which his scheme for a City textile centre deserved, the City would to-day again be the greatest textile market of the world.

[Sir Ernest concluded by showing a range of woven silk and other furnishing fabrics from 1850 to the present day*.]

* * *

I would like to acknowledge my great indebtedness and express my warmest thanks to Mr. Robin Baker of Swaisland's Fabric Printing Co., Mr. Roy Hind of David Evans & Co. Ltd., and Mr. Hilary Blackmore of Liberty & Co. Ltd. for giving me particulars of their firms' printworks and lending me some precious samples; to Mr. Peter Floud and Mrs. B. J. Morris of the Victoria and Albert Museum for lending me some samples from the unique collection of that wonderful Museum's Circulation Department; to my colleague Alec Hunter for letting me use some of the results of his own researches. I have also used the following books—

Blackham, R. J., *London's Livery Companies* (London: Sampson Low, 1931).

Caves, W. T., *Wholesale Distribution* (London: Wholesale Textile Assocn., 1951).

Consitt, F., *The London Weavers' Company* (Oxford University Press, 1932).

"Drapers' Record", *Textile London* [1893].

Warner, Sir Frank, *The Silk Industry* (London, [1921]).

(MS. received 19th March 1953)

* Sir Ernest Goodale is to repeat his lecture and exhibition of fabrics on Thursday, 29th October 1953, at the Victoria Hotel, Bradford (see p. xi).

Fuel Efficiency in the Dyeing and Finishing Industries

W. SHORT

*Meeting of the Scottish Section held at the St. Enoch Hotel, Glasgow, on 9th December 1952,
Mr. R. D. Alexander in the chair*

The Ministry of Fuel and Power has provided an advisory service to all users of fuel since the early years of the 1939–1945 war, when the necessity to save fuel was so suddenly brought to the notice of industrial and domestic consumers. At present the services available can be briefly summarised as follows—

In each region there are skilled demonstrators available who are capable of instructing firemen in the correct methods of firing any type of boiler plant. This is done by practical demonstration on the firm's own plant, and apart from enabling the boiler to be operated more efficiently, these demonstrations very often enable firms to eliminate any smoke nuisance from their chimneys.

Fuel engineers are available to give advice on possible savings that can be made on any type of fuel-using plant, no matter how small. The collective experience of the Ministry's engineers enables assistance to be given to any trade or industry.

Since 1949 the Ministry has been operating Mobile Testing Units, by means of which a large number of recording and other instruments can be rapidly transported to firms and used to carry out detailed heat-balance surveys of boiler, power, and process plants. These surveys have enabled substantial additional savings to be made, even at firms which had stopped the obvious sources of loss that could be detected by visual inspection. For example, the first 45 firms surveyed in Scotland were given reports showing that on average 26% of their fuel could be saved by carrying out recommendations based on the detailed results of the tests. As a result of the work carried out by the Mobile Testing Units, a considerable amount of information of particular interest to the dyeing and finishing trades is now available.

BOILER PLANTS

To start with the boiler plants which are responsible for providing the process steam used, there is the combustion of the solid fuel, which is the most widely used in these industries. A very common fault is to admit too much air through the grates and doors of the furnaces. While it is not possible in practice to use only the theoretical quantity of air required for combustion, the aim should be to use as little excess as possible, since any excess is merely heated and discharged uselessly up the chimney. In fact, especially on the Lancashire type of boiler, too great an excess of air, by spoiling the heat transfer by radiation in the furnace tubes, has a very marked effect on efficiency; and experiments have shown that a Lancashire boiler fitted with a superheater can drop in efficiency from 70% to 60% when the excess of air is increased from 40% to 120%.

These latter figures correspond to 12% and 8% respectively of carbon dioxide in the gases leaving the boiler, and every effort should be made to maintain carbon dioxide figures between 10% and 12%. It is extremely difficult for the firemen to estimate the combustion conditions, and installation of carbon dioxide indicators or recorders would be a profitable investment on boilers burning any appreciable tonnage of fuel.

The next point is the load carried by the boilers. Frequently inspections reveal that, where several boilers are in use to carry the load, each boiler is working at very much below its normal maximum rating. While there are often sound reasons for this, such as poor natural draught or a lower grade of fuel than was used in the past, tests have shown that the efficiency of a boiler falls off below about 60% of the normal rating. It must be stressed, however, that forcing a boiler at, or above, its normal rating also leads to reduced efficiency. As an illustration, boilers of the sizes given in Table I are most likely to give maximum efficiency at the steaming rates quoted, although the condition of flues and scale formation may cause some variations.

TABLE I
Optimum Steaming Rates of Lancashire Boilers

Size of Boiler		Steaming Rate (lb./hr.)
Length (ft.)	Diameter (ft.)	
28	7½	4000–5500
28	8	4500–6000
30	9	6000–8000

When boilers are operated either with an unduly large excess of air or on very high or very low loads, the performance of an economiser, if fitted, is often affected considerably. Several cases have been seen where an economiser was being run with the by-pass damper partly open because without this by-passing the temperature of the water leaving the economiser would be too near that of the water in the boilers for safety. On investigation it was found that the trouble was due to the boiler being operated inefficiently, so that the heat content of the gases leaving the boiler was excessive. The economiser was recovering much of this heat, and heating the water to a dangerously high temperature. By improving the combustion conditions so as to absorb more heat in the boilers themselves, it was found possible to shut the by-pass dampers and still keep the water from the economiser at a safe temperature.

On many of the boilers inspected, the grate areas are much too large. This gives a very low burning rate per square foot of grate, and makes it extremely difficult to maintain good combustion conditions. Usually this low burning rate gives a low firebed temperature, which both reduces the

TABLE II
Steam Consumptions of Open and Enclosed Dyeboxes for Piece Dyeing

	Firm A		Firm B		Firm C	
	Open	Enclosed	Open	Enclosed	Open	Enclosed
"WASH"						
Total steam to wash, lb. ...	—	—	—	—	1041	972
Time taken, min. ...	—	—	—	—	22	25
Steam rate, lb./hr. ...	—	—	—	—	2836	2333
"BOIL"						
Total steam used, lb....	690	690	2217	2017	1328	1522
Time taken, min. ...	35	33	21-6	24-6	35	43
Steam rate, lb./hr. ...	1183	1255	6390	5027	2277	2124
"SIMMER"						
Total steam used, lb....	2850	1614	9030	3228	4240	1605
Time taken, min. ...	180	180	181	209	169	187
Steam rate, lb./hr. ...	950	538	3037	909	1505	516
TOTALS FOR COMPLETE CYCLE						
Total steam used, lb....	3540	2304	11,247	5245	6609	4099
Time taken, min. ...	215	213	202-6	233-6	226	255
Steam rate, lb./hr. ...	988	649	3330	1340	1722	1253
SAVING BY ENCLOSURE, %	—	35	—	53	—	37

heat transfer in the furnace tube of shell-type boilers and often makes it very difficult to avoid smoke. The correct solution is to shorten the grate either by fitting a new bridge and shorter bars or by building a solid extension to the existing bridge on top of the existing bars. As a general rule, for natural draught, the burning rate per square foot should be above 15 lb./hr.; with forced-draught grates it should be at least 20 lb./hr. In this connection it should be pointed out that, with hand firing, the fireman must be very skilled indeed to maintain good combustion conditions on grates more than 5 ft. long. With longer grates there is a tendency to allow the fire to get so thin at the back that much air passes through this rear portion without doing any useful work.

DYEING AND SCOURING PLANT

Much testing* has been done on the piece dyeing of cloth, and at three firms tests were made with ordinary open-type dyeboxes and with the same dyebox fitted with an enclosure so as to cover the upper winch and the cloth above the level of the liquor. This enclosure was not vented or ventilated in any manner while the dyebox was in use, but provision was made by opening panels at front and back for the pieces to be positioned and for samples to be taken.

At the first firm, dyeing light cotton fabrics, 35% of the steam originally used was saved (Table II). At the second firm, dyeing light rayon fabrics, 53% was saved. At the third firm, again on rayon fabrics, 38% was saved, even though the fabrics were given a preliminary wash in the dyebox.

In general, it can be said that the enclosure saves little or no steam while the liquor is being brought to dyeing temperature, but there is a very marked reduction in the steam required during the simmering period, so that generally the percentage saving increases with increased time of simmering. In the first case an automatic temperature controller was fitted to the dyebox, which probably

accounts for the smaller saving obtained by enclosing compared with the other two firms, where control was by hand. In all these three cases fairly low-pressure steam (20–40 lb./sq.in.) was used in the dyeboxes; if high-pressure steam is used to heat water by direct injection, there is considerable risk of large bubbles of steam being formed when the water is hot, and these rise to the surface before they are completely condensed, allowing a considerable amount of steam to be wasted. If the steam is superheated when it enters the dyebox the loss is even greater; and while superheat in steam is an advantage for distribution to prevent excessive condensation in the main pipes, it is recommended that only a small amount be given to process steam, just sufficient to meet the mains losses, so as to yield dry saturated steam at the point where it is actually used. Similar remarks apply to drying plant using steam heaters or coils, where superheated steam gives a reduced heating rate compared with saturated steam.

TABLE III
Steam Consumption of Obermaier Open Dye Vats used for Dyeing Rags

Vessel ...	A	B
Diameter of vessel, ft. ...	5	5
Liquor capacity, gal. ...	185	300
Type of control ...	Hand	Robot thermostatic
Total steam used per cycle, lb. ...	2388	1337
Time for dyeing cycle, min. ...	88	63
Weight of rags dyed, lb. ...	380	500
Weight of steam used per lb. of rags dyed, lb....	6-28	2-67

Table III shows results obtained by the use of automatic thermostatic control equipment of rag dyeing. The equipment regulated both the time and the temperature of the various portions of the dyeing cycle, and the results obtained are compared with those obtained with a similar dye vat (at the same firm) which was controlled by hand only. These particular dye vats were of the Obermaier

* All the figures quoted in what follows have been obtained during surveys by Mobile Testing Units.

type with pump circulation and direct injection of steam, which in this particular case was used at 45 lb./sq.in. The striking savings achieved will encourage those responsible for similar dyeing processes to install such automatic control equipment.

TABLE IV
Steam Consumption of 24-can Stainless-steel
Top (Slubbing) Dyeing Machine

(These figures do not include steam used for mixing dye liquor)

	Open	Totally Enclosed
Weight of slubbing dyed, lb. ...	250	322
"WARMING-UP" PERIOD		
Steam used, lb. ...	107	113
DYEING PERIOD		
Steam used, lb. ...	293	267
Steam rate, lb./hr. ...	382	298
CHROMING PERIOD		
Steam used, lb. ...	247	213
COMPLETE CYCLE		
Total steam used, lb. ...	647	593
Steam used per lb. of slubbing, lb. ...	2.52	1.84
Total time for cycle, min. ...	122	131

Table IV indicates the saving that can be obtained in slubbing or top dyeing. The machine on which the tests were made was a 24-pot stainless-steel type with pump circulation and direct steam injection at 17 lb./sq.in. It will be seen that, when the machine was run with a close-fitting lid, there was an appreciable saving, due to the reduced heat loss from the liquor.

Table V shows results obtained on a typical set of enclosed stainless-steel hank dye vessels, fitted with reversible propeller-type circulation and heated by direct steam injection. The figures also serve as an illustration of the possible economies that can be obtained by using warm water instead of starting the dyeing from cold. In many dyeing processes there can be no objection to supplying water at 120–140°F., instead of cold water, to the dye vessels. If water is supplied at 120°F. instead of 50°F., there is a saving of about 40% of the steam used in the dye vessel for raising to the "boil". As this particular portion of the dyeing cycle is the usual cause of the peak steam demands

TABLE V
Steam Consumption of Hank Dye Vessels
(Knitting Wools)

	A	B	C
INITIAL BOIL (only partly filled)			
Water added, gal. ...	200	140	75
Time steam used, min. ...	20	15	15
Quantity of steam used, lb. ...	400	270	150
<i>Fill to working level, enter hanks—</i>			
DYEING RUN			
Water added, gal. ...	450	280	175
Time steam used, min. ...	65	60	45
Quantity of steam used, lb. ...	920	680	350
SECOND BOIL (no further addition of water)			
Time steam used, min. ...	15	10	8
Quantity of steam used, lb. ...	170	90	60
TOTALS FOR COMPLETE CYCLE			
Total steam used, lb. ...	1490	1040	560
Weight of dry wool dyed, lb. ...	150	120	60
Quantity of steam per lb. of wool dyed, lb. ...	9.9	8.7	9.3

in the dyehouse, such a reduction means that, if the time taken to raise the liquor to dyeing temperature remains unchanged, the peak loads in the boilerhouse can be reduced by about the same percentage. It can thus be seen that, for a boiler plant that is genuinely overloaded at peak steam-demand periods, a case could be made out for the installation of a hot-water storage tank heated by live steam during periods of low steam demand. This would be much cheaper to instal than a steam accumulator, and would give a similar smoothing out of the steam demand from the boiler. However, it is not usually necessary to contemplate using live steam for heating water, since there is no reason why use should not be made of the heat in the dyehouse effluent. In many dyeing processes, at the end of the dyeing cycle the dyeing liquor is discharged to drain at, or very near, boiling point. If steps are taken to ensure that any cold water used for washing or rinsing purposes is discharged to a separate channel, it is possible to collect all the hot effluent. Two suggested systems of

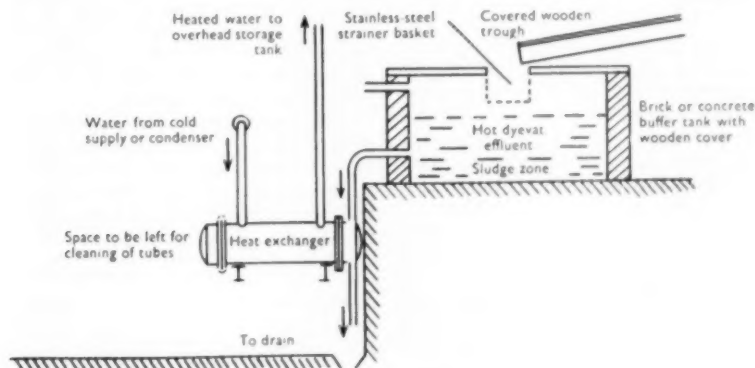


Fig. 1—First Suggestion for Recovery of Heat from Hot Effluent

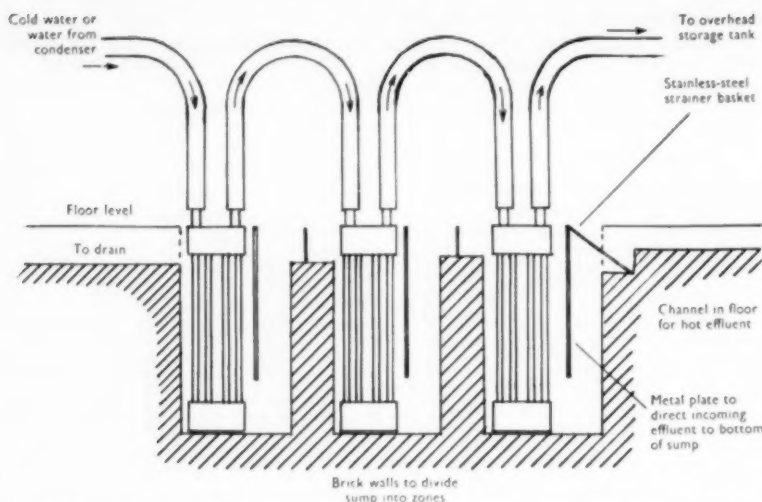


Fig. 2—Second Suggestion for Recovery of Heat from Hot Effluent. The elements consist of batteries of plain tubes coupled together in series by flexible connections. A suitable hoist should be arranged above the tank, so that each element can be lifted out of the tank and cleaned by a high-pressure jet of water. The brick walls serve to keep the hottest effluent in contact with the hottest water in the elements.

recovering heat from this effluent are shown in Fig. 1 and 2, and of course there are many proprietary types of heat exchanger available that are suitable for this purpose. The essential requirements are—(i) some storage capacity must be included in the scheme to give a reasonably steady recovery of heat from the intermittent discharges of hot effluent from the dye vessels; (ii) a method of straining should be incorporated to remove the larger particles of material or sediment; and (iii) the heat exchanger itself should be of such a design that the surfaces in contact with the effluent can easily be cleaned.

A similar case can be made out for installing such a heat exchanger in cloth-scouring departments, where cold water is usually heated by live steam to 120–130°F. for scouring purposes and after use is run to drain. At one firm recently investigated the average temperature of such water going to drain was found to be 125°F.

Cooling water from surface condensers of turbine or engine plant could be used instead of cold water, and could ideally be linked with such a heat exchanger scheme as described above. Many firms still have mill engines fitted with jet condensers; there is the possibility of using most of the jet condenser water for process work such as scouring or dyeing in such cases. When this is first suggested, dyers invariably mention the possibility of such water being contaminated with oil. However, if the portions of the engine in contact with the steam were lubricated with, say, colloidal graphite, there would be no possible carry-over into the condenser. Alternatively, this fear of oil contamination could be overcome by a combination of an oil separator in the exhaust steam line to the condenser and a settling tank for the condensate, to allow any oil to rise to the surface, while warm water is drawn from near the bottom of the tank.

If the demand for hot water exceeds the supply from the jet condenser, further economies could be made by deliberately reducing the engine vacuum so as to get hotter water from the condenser. While this would cause a small rise in the steam used by the engine, the rise would be less than the live steam required to heat the condenser water to the higher temperature. If a condensing engine can be used in this way, the fuel savings obtained are comparable with those obtained by use of a back-pressure engine.

BLEACHING KIERS

Table VI shows results obtained during the operation of bleaching kiers. The first set of results illustrates the saving to be made by the insulation of kiers in the linen trade. The second set shows the remarkable savings obtainable in yarn bleaching by replacing old "open" kiers by pressurised kiers with pump circulation. The third set of results was obtained on kiers used for bleaching canvas or sailcloth, and again shows that savings can be made by using modern kiers. In this last case, the original kiers were pressurised, but steam was the only circulating medium. The more efficient kiers incorporated pump circulation and thermostatic control.

The remarks made above regarding the recovery of heat from the hot dye-vessel effluent apply with equal force in the case of these kiers, as here also the use of warm water to fill the kiers would reduce the peak steam demand while the temperature is being raised to simmering.

DRYING EQUIPMENT

Finally, we may consider briefly the drying of yarn and material after the wet processing itself has been carried out. The first point that should be stressed is the removal of as much water as possible by mechanical means, e.g. hydroextractors or

TABLE VI
Performance of Bleaching Kiers

Kier No.	Description of Kiers	Liquor Vol. (gal.)	Dry Wt. of Material (cwt.)	Time taken (hr.)	"Boil" Steam used Quantity (lb.)	Rate (lb./hr.)	Time taken (hr.)	"Simmer" Steam used Quantity (lb.)	Rate (lb./hr.)	Total Steam used—Quantity (lb.)	Per lb. of Material (lb.)
BLEACHING OF LINEN CLOTH											
A 8	Uninsulated. Pump-circulated closed type with external tubular heat exchanger	2000	60	3-31	4840	1460	13-0	2215	170	7055	1-05
A 3	Uninsulated. Pump-circulated closed type with steam injection into discharge line of circulating pump	2000	60	4-09	4580	1120	10-7	1820	170	6400	0-95
A 4	Insulated. As A 3	2000	60	5-10	4460	875	9-9	1487	150	5947	0-88
WASHING AND BLEACHING OF HEMP YARN											
B 1	Uninsulated. Heated by steam injection, which also provides circulation. Loose-fitting cover only	600	10	0-5	1210	2420	2-0	2240	1120	3450	3-08
B 2	Insulated. Pressurised with pump circulation. Heated by direct injection of steam	600	10	0-5	400	800	2-0	46	23	846	0-76
BLEACHING OF SAILCLOTH											
C 1	Heated by steam injection, which also provides circulation. Fitted lid to allow simmering at 5 lb./sq.in.	650	25	2-0	—	—	8-0	—	—	4154	1-48
C 2	Pressurised; heated externally via calorifier with pump circulation and thermostatic control for simmering at 260°F.	1270	43	3-0	—	—	9-0	—	—	3850	0-80

TABLE VII
Performances of Various Driers used in the Textile Trades

Type of Drier	Dried Through-put (lb./hr.)	Moisture evaporated (lb./hr.)	Steam used—Rate (lb./hr.)	Per lb. of Moisture (lb.)	Remarks
RAG DRYING					
Continuous-tunnel type, 45 ft. long, with brattice conveyor 5 ft. wide; internal heaters and circulating fans ...	575	484	1003	2.07	Average performance for this type
HANK DRYING					
Pole-type hank drier, single-pass continuous-tunnel type 40 ft. long; internal heaters and fans ...	2010	367	956	2.61	Steam consumption appears high owing to relatively low initial moisture content of wool. Relatively low moisture content in exhaust air
Pole-type hank drier, two-pass tunnel type; internal heaters and fans ...	1170	866	1040	1.20	Good performance due to good insulation and control of exhaust air to prevent excessive throughput and maintain high moisture content
PIECE DRYING					
28-can drier, horizontal two-layer type ...	450	356	1350	3.80	Poor, owing to intermittent loading
32-can drier, horizontal two-layer type ...	400	345	467	1.35	Good performance due to intelligent operation. Drier kept running fully loaded at moderate speed with very low steam pressure input
Rough drier, cloth held against travelling brattice by pressure of air from batteries of nozzles; internal heaters and fans ...	250	251	754	3.00	Poor, as drier much wider than pieces being dried
Rough drier, as above, but different make ...	240	280	550	1.96	Better than above, as width more suitable and air circulation more positive
Stenter, 90 ft. single-pass type, unenclosed, with hot air boxes above and below cloth, fed from external tubular heater; no recirculation ...	550	405	2810	6.93	This is a very bad performance, owing almost entirely to lack of recirculation, resulting in the use of a large excess of hot air passing to room in which machine is situated
Stenter, 72 ft. single-pass type, enclosed with 8 fans and heater batteries working with total recirculation, and one small exhaust fan ...	280	183	450	2.46	This is an average performance for this type of drier. Main differences from stenter above are enclosure of machine and internal recirculation of air

squeeze rolls, since it is much cheaper to remove moisture in this manner than by evaporation in driers.

It must be borne in mind that, in the case of a hot-air circulation type of drying machine, the steam consumption is fairly constant whether or not any material is passing through. Many cases have been seen where circulating fans have been left running and steam valves left open at lunch periods or during temporary hold-ups in the flow of material to the drying department. It is urged that, if the operator will not assist in fuel economy by shutting down the drier when it is not actually in use, some system of interlocking should be considered. For example, on many driers it should be possible to interconnect the circulating and exhausting fans with the material-feeding mechanism, so that when no material is being fed the fans are stopped.

In many driers tested, too much air is entering and leaving, with the result that the moisture contained by each pound of hot air leaving the drier is only a small proportion of the possible amount. In such cases, readings should be taken on wet-and-dry-bulb hygrometers, and the amount of exhaust air reduced until a reasonably high humidity is obtained. Care should be taken to ensure that no hot air is leaving the drier through unduly large material entry and exit openings or through damaged panels in the drier casing. In driers where at present the only heat input is by incoming fresh air passing through a heater unit, it is almost certain that excessive air changes are occurring, as can be confirmed by humidity readings on the exhaust air. In such cases a duct should be built so as to recirculate most of the exhaust air into the inlet of the fan supplying the

heater battery. Examples have been found where "total recirculation" has been carried out by such a duct and the drier has still operated successfully, as the amount of air entering and leaving through the material entrance and exit slots has been ample to give a satisfactory air change.

In the drying of textile fibres, as a general rule, the drying rate increases with the speed of the hot air passing over or through the material. There is a limit to this, but it is not usually reached in the average type of drier. As a result, the drier should not have any large idle volumes, and the air passages over the material should be as small as possible to ensure high speed of movement with a relatively small total quantity of air. Driers of the stenter type used both to dry cloth in piece form and to set it to width are often found either operating in a large room, or having a very large casing built round them. It is suggested that in both cases too great a volume of air is being heated, much of which is never made to come into close contact with the moist cloth.

Table VII indicates the ranges of performance found by tests on different types of drier.

* * *

It is to be hoped that this account has suggested methods by which economies can be achieved in the dyeing and finishing industries. The figures quoted have been selected from a very large number of tests carried out all over Great Britain by Ministry engineers, and were chosen to illustrate definite economies that were obtained by modification of existing plant, or where this was not practicable, by installation of new plant capable of more efficient operation.

(MS. received 24th December 1952)

COMMUNICATION

Polymerisation of a Series of Vinyl Monomers in Wool

N. K. BOARDMAN and M. LIPSON

A series of acrylates and methacrylates were polymerised in wool by free-radical initiation from aqueous methyl alcohol. A direct relationship was observed between the hardness of the polymer and its effect on the elastic properties of single fibres; the harder polymers increase the work of extension, whilst the softer polymers decrease it. Some surface deposition occurs and increases the frictional properties of the fibres, again in correlation with the hardness of the polymer. Polymethyl methacrylate gives a satisfactory degree of washing shrinkage control, but large quantities are required; the effect is probably due mainly to surface deposition of excess of polymer.

1. INTRODUCTION

Speakman, Stott, and Chang¹ concluded that for milling shrinkage to occur a fibre must have surface scales, be easily deformed, and possess the power of recovery from extension. On this basis, resins may decrease shrinkage by masking the scale structure, by altering the work required to stretch the fibre, or by decreasing the power of recovery from extension. A deposit of polymer may also prevent felting by interfibre bonding².

Most attempts to shrinkproof wool by resin application have been confined to external deposits of polymer on the fibre, where the non-felting effect results from alterations in surface frictional properties and interfibre bonding³. As deposits of

resin inside the fibre are less likely to affect the appearance and the handle of a fabric, efforts have been made to form polymers within the fibres⁴⁻⁶. Thus, internal deposits of vinyl polymers have been synthesised from aqueous solutions of monomers, ferrous iron and hydrogen peroxide being used as catalyst⁶. To form the polymer the wool was impregnated with a dilute solution of ammonium ferrous sulphate and then treated with a solution of monomer containing hydrogen peroxide. Preferential internal polymerisation was brought about by free hydroxyl radicals formed inside the fibres. With a water-soluble monomer, such as methacrylic acid, large quantities of polymer could be synthesised in this way within the fibres.

Emulsion polymerisation of methyl methacrylate, however, tended to produce surface deposition of polymer on the fibres. Methyl methacrylate and methacrylic acid were copolymerised from solution in aqueous methanol with little evidence of surface deposition.

In the foregoing experiments, large amounts of polymer were required to produce unshrinkability. Obviously, for a treatment to have commercial application, small quantities of polymer would be desirable. The present investigation extends the work to other monomers by examining the effects of internal deposits of a series of vinyl polymers having varying mechanical properties on the elastic, frictional, and shrinkage properties of wool.

2. EXPERIMENTAL

(a) Materials

The monomers were stabilised samples of pure products kindly supplied by the Rohm & Haas Co., U.S.A. Each was distilled immediately before use.

Measurements of swelling, elastic properties, and scaliness were carried out on Lincoln wool fibres, whilst merino wool was used for the determination of weight increases due to polymer deposition. The root ends of staples cut from the respective fleeces were purified by Soxhlet extraction with petroleum ether (8 hr.) and ethanol (6 hr.) followed by six changes of distilled water at 50°C.

The fabric for shrinkage tests was a 64s-quality wool of the following structure—

Warp	...	33s Yorkshire skeins, 32 ends/inch
Weft	...	30s Yorkshire skeins, 30 picks/inch
Weave	...	Mayo twill.

Samples measuring 4 in. × 4 in. (2.5 g.) were purified by extraction with ether, alcohol, and distilled water as described above.

(b) Method of Polymerisation and Tests

The loose wool (0.5 g.) was pretreated in 10 ml. of 0.2% ammonium ferrous sulphate for 2 hr. at 25°C., squeezed, and allowed to dry at room

TABLE I
Effects of Various Polymers on Elastic Properties of Wool

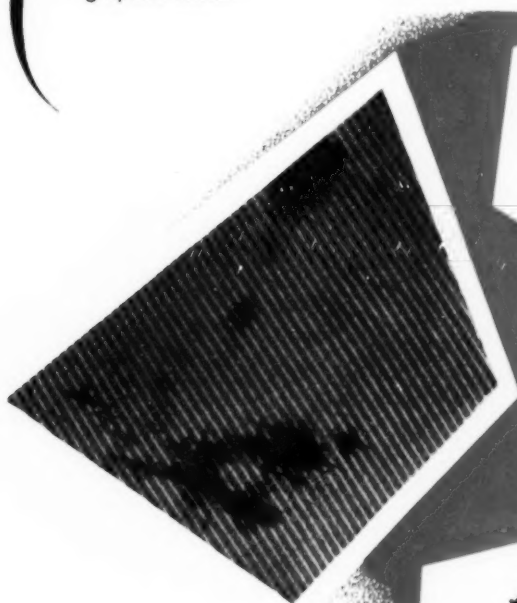
Monomer (ml.)	CH ₃ OH (ml.)	H ₂ O (ml.)	0.2-vol. H ₂ O ₂ (ml.)	Time (hr.)	Weight Increase (%)	30% Index*
0	4	5	1	6	—	-2, -2
METHYL METHACRYLATE						
0.5	4	5	1	1.5	8.1	0
0.5	4	5	1	2	24	19, 50
0.5	4	5	1	2	32	17, 13
0.5	4	5	1	2	36	16, 19, 13
0.5	4	5	1	3	46	41
0.5	4	5	1	3	57	52, 32
ETHYL METHACRYLATE						
0.5	5	3	1	3	31	7, -4
0.5	5	3	1	3	45	48, 17
0.5	5	3	1	6	37	35, -6
0.5	5	3	1	6	52	8, 9
0.5	5	3	1	6	52	14
0.5	5	3	1	6	65	-13
n-BUTYL METHACRYLATE						
1	6.5	0	2	2.75	106	8, -2
1	6.5	0	2†	5	107	2
1	6.5	0	2	3	85	-3, -5
1	6.5	0	2	3.5	108	-1, -5
1	6.5	0	2	4	109	-1
0.5	6.5	1	1	4	21	4
1	6.5	0	2†	5	87	16
0.5	6.5	0	2	6	101	-12, 0
0.5	6.5	1	1	6	53	8, -6
METHYL ACRYLATE						
0.75	3.75	9	1.5	3.5	47	0, -3
0.5	2.5	6	1	5	64	-13
0.5	2.5	6	1	3	49	0, -17
0.5	2.5	6	1	6	64	-3
ETHYL ACRYLATE						
0.5	3.5	5	1	6	65	-12, -23
0.5	3.5	5	1	6	47	-13
0.5	3.5	5	1	6	50	0
0.5	3.5	5	1	6	71	-21, -43
0.5	3.5	5	1	6	25	-8, -24
0.5	3.5	6	0	6	0	0

* Alteration in work required to extend fibre 30% in water

† 0.5-vol. H₂O₂

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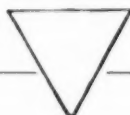
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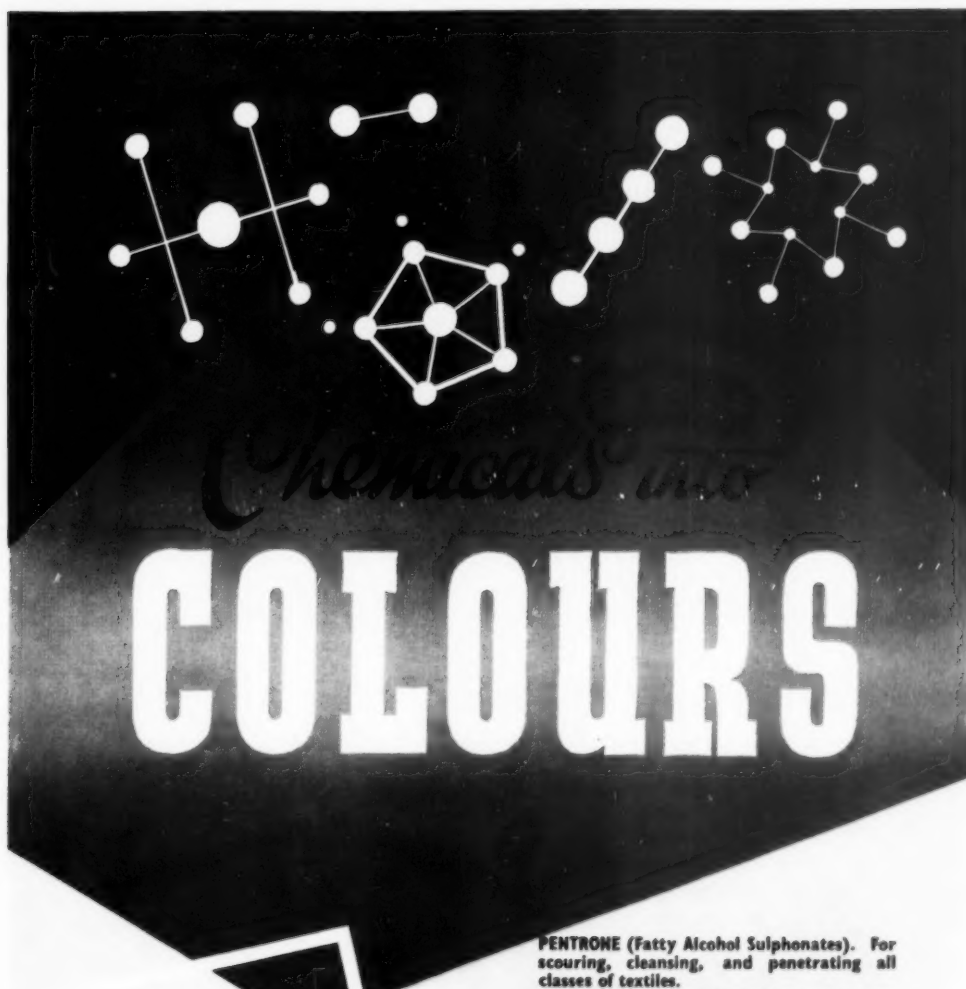
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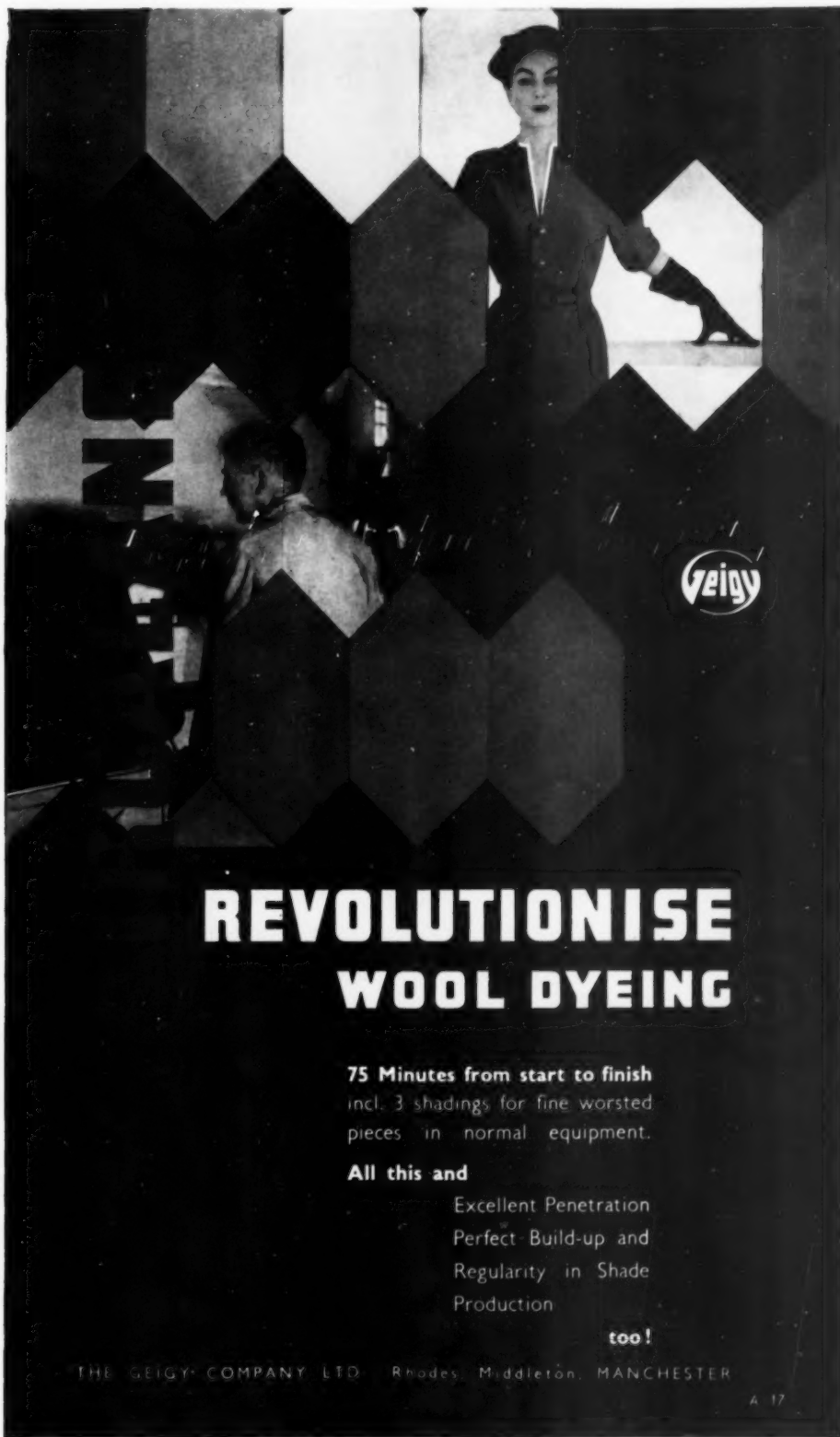


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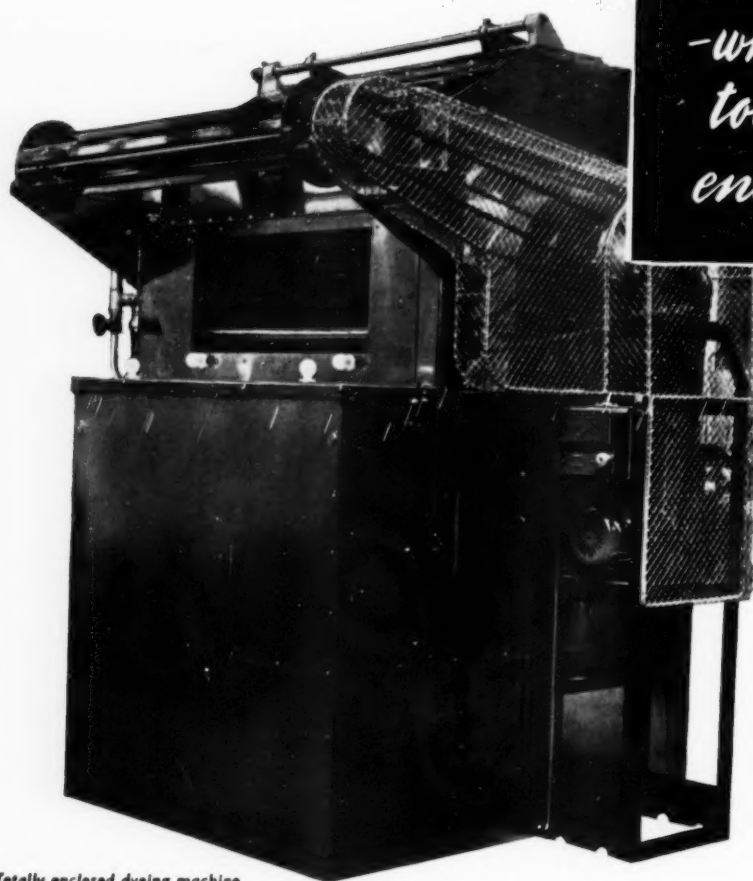
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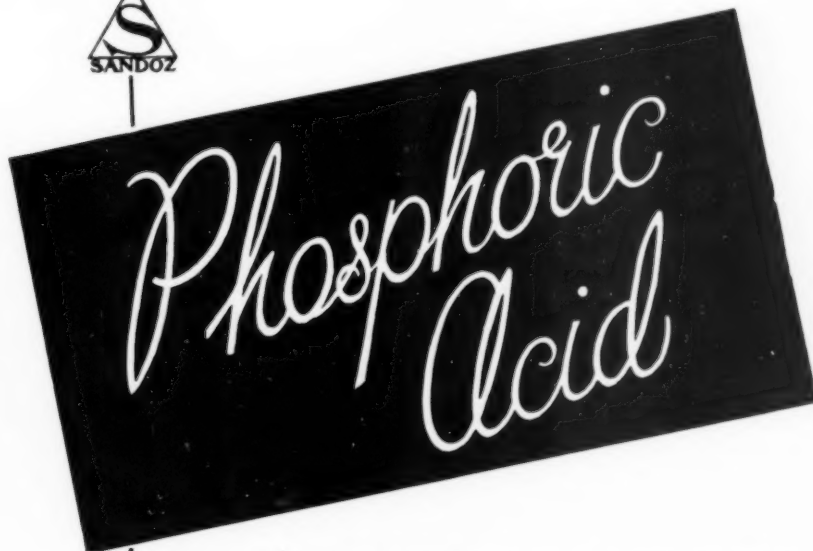
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temperature. It was then treated at 50°C. in an aqueous-methanolic solution of the monomer containing hydrogen peroxide. The quantity of polymer deposited was controlled by varying the concentration of monomer and the time of treatment. To assist absorption of the monomer, the maximum possible amount of water was used in each solution. Treatments were carried out for varying times with different quantities of monomer and hydrogen peroxide; details of the conditions are given later with the results. After treatment, the wool was washed in several changes of methyl alcohol and then overnight in running water. The increase in weight due to polymer formation was ascertained by weighing the wool conditioned before and after treatment at 22°C. and 65% R.H.

Lincoln fibres previously calibrated by 30% extension in water at 22°C. on the Cambridge extensometer were included in the above treatments to determine the effect on elastic properties. The effect on scaliness was similarly ascertained by frictional measurements in 0.5% soap solution at 35°C. on fibres before and after treatment, the capstan method⁷ being used. Swelling due to internal deposition of resin was determined by fifty equidistant measurements of diameter along a 2.3 cm. length of fibre before and after treatment.

For felting shrinkage tests, fabric samples (2.5 g.) were treated in five times the amounts of solutions used for loose wool; washing was carried out in 0.05% soap solution in a rotary machine⁸.

3. RESULTS AND DISCUSSION

Table I records the effects of different percentages of the various polymers on the elastic properties of single fibres. Variations between duplicates in the same treatment probably result in part from differences in the amounts of polymer formed in individual fibres. A similar effect has been previously observed in the polymerisation of methacrylamide from aqueous solutions⁶. Despite this, significant differences can be recognised between the groups. Polymethyl methacrylate gives appreciable increases in work of stretching when present to the extent of 20% or more; polyethyl methacrylate causes smaller work increases, whilst polybutyl methacrylate brings about very little increase. The increases are in the same order as the softening temperatures and the Pfund hardness figures of the resins^{9, 10}. Acrylates, which are softer resins than methacrylates, tend to have a weakening effect on the wool. Formation of polymer in the fibre probably reduces resistance to extension by breaking hydrogen bonds between polypeptide chains; the harder resins can mask this effect by the greater mechanical hardness of the polymer.

Fig. 1 and 2 show typical stress-strain curves for fibres containing large amounts of polymethyl methacrylate and polyethyl acrylate respectively. Polymethyl methacrylate increases both work of extension and resistance to recovery. The fibres do not return to their original lengths immediately, but do so on relaxation in water for 24 hr. Polyethyl acrylate considerably alters the shape of the stress-strain curve, and almost completely eliminates the normal Hookean region.

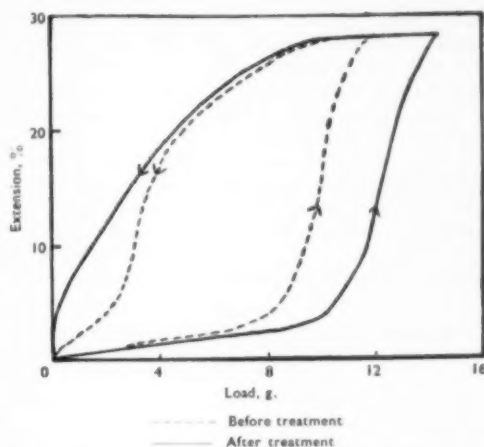


Fig. 1—Effect of Polymethyl Methacrylate on Load-Extension Curves of Single Wool Fibre

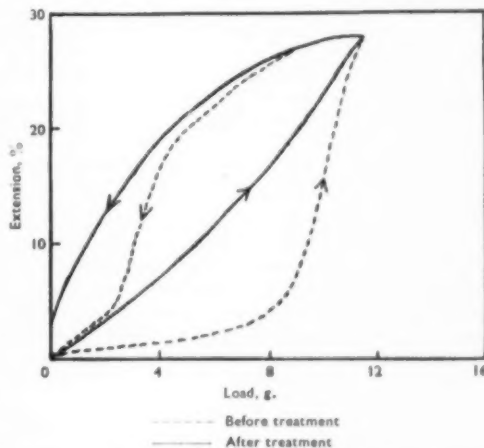


Fig. 2—Effect of Polyethyl Acrylate on Load-Extension Curves of Single Wool Fibre

The profound effect of such polymers on elastic properties could result only from resin deposition within the fibre structure. This is supported by the swelling which occurs when large amounts of polymer are present in the fibre. Table II records the mean increases in fibre diameter resulting from deposition of varying amounts of polymethyl methacrylate.

TABLE II
Fibre Swelling due to Polymethyl Methacrylate

Increase in Weight (%)	Increase in Diameter (%)
16	0
19	5
21	4
28	6
32	8
50	24
59	29

It is seen that weight increases of the order of 20% are required to produce any fibre swelling,

which then becomes greater with increasing polymer content. This agrees with the results of Barr and Speakman⁴ on the vapour-phase polymerisation of ethylene sulphide. Their experiments have shown that 20% of free space is present in the fibre to accommodate polymer without dimensional alteration. Swelling can then take place to permit formation of further quantities within the fibre.

The effect of the resins on the scaliness of single fibres is recorded in Table III. Each figure represents the mean of several determinations on different fibres before and after treatment.

TABLE III
Effect of Polymers on Frictional Properties

Monomer	Weight Increase (%)	Before Treatment		After Treatment	
		μ_1^*	μ_2^\dagger	μ_1^*	μ_2^\dagger
Methyl methacrylate ...	46	0.35	0.24	0.51	0.30
	51	0.48	0.28	0.63	0.48
	58	0.43	0.24	0.59	0.43
Ethyl methacrylate	46	0.26	0.18	0.52	0.23
	70	0.36	0.18	0.42	0.31
Butyl methacrylate	17	0.32	0.23	0.34	0.24
	53	0.33	0.21	0.38	0.22
Methyl acrylate ...	49	0.28	0.19	0.35	0.25
	65	0.25	0.18	0.38	0.25
Ethyl acrylate ...	28	0.27	0.18	0.30	0.23
	62	0.39	0.21	0.39	0.26

* μ_1 = Anti-scale coefficient

† μ_2 = With-scale coefficient

Some surface deposition of polymer has in most instances caused increases in the values of frictional coefficients. The increases are greater with harder resins such as polymethyl methacrylate than with the softer resins such as polybutyl methacrylate and polyethyl acrylate.

TABLE IV
Washing Shrinkage of Fabrics

Polymer	Area Shrinkage (%)
Weight, % on untreated wt.	30 50
Control (untreated) ...	40 40
Methyl methacrylate ...	15 6
Ethyl methacrylate ...	16 10
Butyl methacrylate ...	33 28
Methyl acrylate ...	25 15
Ethyl acrylate ...	21 15

Table IV shows the area shrinkages on washing fabrics containing 30% and 50% respectively of each of the various polymers.

Large amounts of polymer are required for satisfactory shrinkage control, the best result being obtained with methyl methacrylate. Comparison of Tables I and IV, however, shows that shrinkage reduction cannot be correlated with increase in work required to stretch single fibres. Thus the acrylates show appreciable shrinkage reduction when present in large amounts, and yet they decrease the work required to stretch individual fibres. Any reduction in felting properties probably results from external deposition of some of the polymer causing increases in interfibre friction as shown in Table III. With methyl methacrylate, the internal deposit of polymer may also play a part in decreasing felting. Previous workers have observed^{8,11} that harder polymers are more effective than softer polymers in reducing the felting properties of wool by surface application. It would appear, therefore, that the physical properties of the polymers deposited on the surface of the fibres in the present experiments mainly account for the differences in effects on felting properties. The only polymer giving a satisfactory degree of shrinkage control is polymethyl methacrylate, but the large quantities required would preclude this as a possible practical method of rendering wool non-felting.

Thanks are due to Mr. A. R. A. Backwell for valuable experimental assistance.

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION
WOOL TEXTILE RESEARCH LABORATORY
GEELONG
AUSTRALIA

(Received 17th February 1953)

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Notes

Meetings of Council and Committees August

Council—No meeting

Publications—18th

Colour Index Editorial Panel—26th

Deaths

We regret to report the loss by death of Messrs. F. Allison and S. A. Bray.

Rayon Fabric Dyers' and Finishers' Exhibition

The Rayon Crêpe Dyers' Group, the Spun Rayon Fabric Dyers' Group, the Flat Dyed Rayon Association, and the Association of Co-licensees in conjunction with the British Rayon and Synthetic

Fibres Federation held an exhibition of the Dyeing and Finishing of Rayon Fabrics in the Federation's premises, 138 Piccadilly, London W.1, from 26th February to 18th March 1953 and in the College of Technology, Manchester, from 16th to 30th June 1953. The exhibition had the threefold purpose of showing the vital rôle played by dyeing and finishing in rendering rayon and synthetic fibres both attractive and fit for their ultimate use, some of the problems which the dyer and the finisher have to overcome in the processing of these fabrics, and some of the newer finishes.

The exhibition was noteworthy in that it was the first time that such an exhibition had been staged by the dyeing and finishing trade as a co-operative whole and not by individual interests. c o c

New Books and Publications

The Dynamical Character of Adsorption

By J. H. de Boer. Pp. xv + 239. Oxford: Clarendon Press, 1953. Price, 30s. 6d.

The author's aim in this book is to create a mental picture of the molecules adsorbed on a surface in contact with a liquid or gas. We can clearly visualise the molecules lying flat on the surface, to which they may be more or less securely anchored or over which they may be moving freely. When there is a danger of overcrowding they obligingly stand up on end to make room for more, but if this does not suffice, some molecules which cannot find a place on the surface have to sit on the heads of those already there. The author goes to a great deal of trouble to help the reader to appreciate the size of a molecule and to grasp the significance of the large numbers involved in talking about them. His statements are illustrated by a picture, magnified 32 million times, in which the molecules are represented by super bees. This earlier part of the book should appeal to the general reader, for whom presumably it is mainly intended.

The later chapters are more for the specialist in the field of surface adsorption. The linear, Langmuir, and B.E.T. types of isotherm are derived by kinetic arguments, and the assumptions underlying each of them are examined. The author then considers the layer of adsorbed molecules as a two-dimensional gas obeying the van der Waals type of equation, and the consequences of this for the several aspects of adsorption are worked out in great detail. Just as in the three-dimensional case, we may have departures from ideal-gas behaviour, condensation, and critical point phenomena. Isotherms are deduced from the van der Waals equation for unimolecular adsorption on homogeneous and composite surfaces and also for multimolecular adsorption. Calculations show how the shape of the isotherm is affected by different combinations of constants arising in the theory and corresponding, for example, to different energies of interaction between the molecules and the surface

and between the molecules themselves. The results of the calculations are illustrated by numerous graphs. Such comparison with experiment is largely of a tentative nature, since many of the constants are as yet unknown.

This is essentially a book of ideas, and the author's hope is that it will stimulate further research and encourage more experimental work. In many respects the book is tentative, and includes much hitherto unpublished work. Those who agree with the author's approach will welcome the publication of many untried ideas. There will doubtless be others who will deprecate such an elaborate theoretical structure on such slender experimental foundations. The author disarms criticism on these grounds, however, in his final remarks, for he is clearly aware that his picture will need considerable modification as the subject develops.

Apart from one or two obscure paragraphs the writing is extremely lucid. There are a few misprints and grammatical errors, but otherwise the reproduction is up to the usual high standard of the Clarendon Press.

J. CRANK

Symposium on Statistical Methods for the Detergent Laboratories

Presented at a Meeting of Committee D-12 on Soap and Other Detergents, New York, N.Y., 18th March 1952. *ASTM Special Technical Publication* No. 139. Pp. v + 38. Philadelphia: American Society for Testing Materials, 1953.

This booklet contains three papers on the application of statistical methods to detergency investigations. The usefulness of such techniques in detergency, with an example of the employment of the analysis of variance, was described some four years ago in a paper from the laboratories of the British Launderers' Research Association. The introduction to the booklet under review reiterates

the need to use statistical methods in techniques which are subject to chance variation or which must be correlated with practice.

The first paper introduces the ideas of standard deviation, graphical methods of analysis, and tests of significance. The assumption is made that washing efficiency values obtained by washing soiled swatches in a Laundromat have a normal distribution, whereas many more observations than those given are necessary to show this to be so. The use of graphical methods is illustrated by the comparison of the washing efficiencies of two detergents.

The second paper describes the design of the laboratory control of laundry washrooms based on an analysis of variance. The tensile strengths, *inter alia*, of test-pieces washed in different laundries were determined, and from an analysis of the results the variances due to the different laundries, to differences between the test-pieces, and to the methods of testing were found. Hence it was possible to suggest the number of test-pieces to be used, and tests to be carried out, in order to obtain results of a given precision in the most economical way.

The last paper deals with the application of statistical methods of correlation analysis to the problem of comparing the results of laboratory tests for evaluating detergents with the results obtained under more practical conditions. It is pointed out that for quantitative correlation analysis a sufficient number of paired observations is desirable.

It will be apparent from the foregoing that the booklet's chief value for those unfamiliar with statistical techniques will be to arouse interest, so that some standard texts may be consulted; for those with a knowledge of these techniques the papers describe some interesting applications.

R. E. WAGG

Ink and Paper in the Printing Process

By A. Voet. Pp. xii + 213. New York and London: Interscience Publishers, 1952. Price, \$5.90.

There are a few excellent standard textbooks dealing with the manufacture and properties of paper, and at least two in the English language on the technology of printing inks, but the book under review is to be commended as the first major attempt to bring ink and paper together in a scientific treatise. Dr. Voet is well known in printing ink and printing research circles for his work on the rheology of inks, the dielectric properties of pigment dispersions, tack, and the penetration of ink into paper. He is to be congratulated on having co-ordinated a large number of comparatively recent investigations related to the interaction of ink and paper, gathered from a widely scattered literature which, for that reason, is not easily accessible to students.

In his preface the author states that the book is intended as an introduction to the physics and chemistry of ink and its interaction with paper in the major printing processes. He adds that certain aspects of inks, such as colour, gloss, and dispersion, have purposely been omitted because reference

books on these subjects are already available, and the best are listed.

The book is divided into two sections. Part I, comprising six chapters, deals mainly with the flow properties of inks and the relation of these properties to the movement and the behaviour of inks on a printing press. The rheology of ink dispersions is covered fairly thoroughly, particular attention being given to the measurement of the consistency of printing inks. Chapter I provides a bare outline of the functions of inks, their methods of drying, and the principles of the three basic printing processes.

Part II, extending to twelve further chapters, is a study of the interaction of ink and paper under the following headings—Characteristics of Discontinuous Reproduction, i.e. reproduction by the half-tone process; Microscopy of Half-tone Printing, this chapter being illustrated with several interesting photomicrographs of prints by different processes on various papers and of cross-sections of such prints; Contrast and Coverage of Ink, with some reference to colour strength; Uniformity of Ink Films; Penetration of Ink into Paper, including the measurement of speed of penetration; Print-through, i.e. show-through and strike-through; Ink Transfer; Picking of Paper, sometimes called "plucking" of a paper surface by a too tacky ink; Offset, the printer's bugbear, which is better termed *set-off*; Physical Drying of Inks; Chemical Drying of Inks; Properties of Lithographic Inks. Author and subject indexes are supplied.

It is a great pity that, so far as this country is concerned, Dr. Voet's praiseworthy effort seems likely to fall between two stools. Few students of the graphic arts have a sufficient background of science to be able to appreciate more than occasional items in the book, and any student would have difficulty in understanding Chapter VI on ink film separation. On the other hand, it is doubtful whether the book is sufficiently detailed for the purpose of the research worker in this field; for example, there is no reference to the early experiments of Pryce Jones and Goodeve on thixotropy. Nevertheless, Dr. Voet has blazed a trail which, it is to be hoped, others will follow.

The book is well produced, except that, like so many post-war American textbooks, it is printed entirely on art paper, which makes any book disproportionately heavy for its size. Art paper is intended for high-quality reproduction of tonal illustrations, of which there are thirty-seven in this book, mostly two to four on a page. It is not suitable as a text paper because its gloss is tiring to the eyes of the reader, and it is not durable enough to withstand the amount of handling one would like to think that Dr. Voet's book might receive.

F. W. CLULOW

Chemical Analysis of Industrial Solvents (Chemical Analysis—Volume VII)

By M. B. Jacobs and L. Scheffan. Pp. xxii + 501. New York and London: Interscience Publishers, 1953. Price, \$10.00 or 80s. 0d.

To attempt to cover the complete range of present-day industrial organic solvents adequately in a volume of some 500 pages is undoubtedly a

difficult undertaking, and it is not surprising that, under those conditions, some aspects of the work will receive rather less attention than they deserve. It is claimed that this book covers three aspects of solvent analysis—(i) assay of a given solvent, (ii) analysis of known mixtures of solvents, and (iii) identification of unknown solvents or mixtures of solvents. The coverage by the chapters on physico-chemical testing, on simple chemical analysis, and on individual solvent specifications is fairly complete, and is in itself a strong recommendation for the book, because considerable data from numerous sources are conveniently collected in one place. However, it is in the analysis of mixtures, both known and unknown, that the treatment is most sketchy. This is unfortunate, because it is in this very difficult aspect of the subject that a book of this nature could be most helpful to the practical chemist.

Although headed "Chemical Analysis . . . Solvents" a book of this nature necessarily contains considerable information on physical methods of analysis. It is rather surprising that so little

reference is made to the uses of chromatography, and that no reference is made to the use of absorption spectroscopy in the analysis of solvents. Information on these procedures might have been of greater value to anyone interested in the analysis of mixed solvents than some of the other physical methods, which in some cases have received rather brief mention.

The book is well indexed and attractively presented. Although the information appears, at times, to have been over-condensed owing to the breadth of coverage attempted, this will be an acceptable first reference for the chemist interested in industrial solvents.

B. W. SWANSON

Textile Recorder Annual 1953

Pp. 211. Manchester: Harlequin Press Co. Ltd.
Price, 30s. 0d.

This book reviews the year's trading in textiles as well as developments in processing and trends in research. It will be useful mainly for the statistics it contains, which give in tables and diagrams a comprehensive picture of the progress of the textile industry in 1952.

C. O. CLARK

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., 68, 23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Drying of Pastes and Slurries. Basf. BP 692,798

Pastes and slurries, e.g. of intermediates and dyes, which are too viscous to be atomised in conventional spray-drying equipment, are fed to a rotating cylinder fitted with projecting pins or bristles, and the fine particles so produced are dried in a stream of hot gases. The rotating cylinder may resemble a steel wire brush, moving with a low angular speed, whose bristles strike the edge of the mouthpiece through which the paste is fed. The bristles are in this way bent back, but on further rotation they snap forward by reason of their resiliency and throw particles of paste into the drying chamber. Or the rotating cylinder may revolve rapidly at a short distance from the inlet feed.

E. S.

Package Dyeing of Nylon Yarn. British Nylon Spinners. BP 693,839

The yarn is wound on to a hard rubber cylinder covered with a sleeve of more compressible rubber, e.g. of cellular structure, the cylinder and the sleeve being perforated to allow dye liquor to be circulated from inside the sleeve through the yarn wound upon it.

C. O. C.

Feeding Cord Fabric to or from a Machine. Dunlop Rubber Co. USP 2,616,188

The fabric is fed to or from a machine by means of a festoon device having an upper and a lower set of rollers. A deflector plate is placed above each roller of the lower set at an angle to the vertical, the lower edge of each plate touching the rising side of the corresponding roller where it is not covered by the fabric. This prevents broken cords from becoming wrapped around the rollers.

C. O. C.

Cylinder Drying Machine. American Viscose Corp. USP 2,616,188

Drying air is supplied to and exhausted from the neighbourhood of each cylinder. This ensures more uniform drying. The machine is especially suitable for drying regenerated cellulose film.

C. O. C.

Felt-hardening Machine. American Felt Co. USP 2,616,152-4

A roller hardening machine of improved efficiency which treats several bats simultaneously at full width.

C. O. C.

Circulating Systems for Web-coating Machines. United States Rubber Co. BP 694,345

A circulating system for a coating liquid in a coating machine comprises a coating roll, a nozzle for applying the liquid to the roll, a reservoir for the liquid, located beneath the nozzle, and a trough beneath the coating roll for receiving excess coating liquid. A surge tank beneath the trough but above the reservoir communicates with the bottom of the trough, a conduit connects the bottom of the surge tank with the reservoir, and a float valve in the surge tank regulates the flow of liquid through the conduit, ensuring a sufficient depth of liquid above the conduit inlet to prevent foaming through air mixing with the liquid as it leaves the surge tank. A polymeric silicone screen in the surge tank surrounds the inlet from the trough in the surge tank, and the float is prevented from completely sealing the conduit from the surge tank to the reservoir, the float thus being made more sensitive to change in liquid level in the surge tank.

S. V. S.

Pouncing Hat Brims. Doran Brothers. BP 692,832

Automatic Control of Laundry Washing and Similar Machines. Baker Perkins. BP 693,045

In a machine automatically controlled by a rotary control card or the like, the various phases of the cycle of processes are indicated by a series of lamps or other indicators arranged in separate circuits connected to the circuit-changing switch. This switch is controlled by the rotary control card or a control card moving in unison with it, the control card having contact fingers co-operating with the switch and connected to the impulse coil, the circuit-changing switch arm, and the release coil. Both coils are energised by the fingers contacting a contact gauge through slots in the card.

C. O. C.

Dry Cleaning. C. Moore. BP 693,289

The hydroextractor and the filter for the used solvent are mounted on a single rigid base, so that the vibration of the extractor is transmitted to the filter, and the solid matter on the filter leaves is shaken off and sinks to the bottom of the filter.

C. O. C.

Garment Forms. A. Freeman (Engineers). BP 693,247

More even distribution of the heat and more intimate and controlled heating are obtained if the form is internally

heated. Preferably the form is filled with a liquid which is heated electrically. C. O. C.

Garment Press. Kleindienst & Co. BP 693,534

A press which does not produce "squeezed spots" or "shining spots" on the seams of garments, pocket edges, etc. C. O. C.

Automatic Application of Transfers to Glass, Ceramics, and the like (IX p. 354).

Microfiltration with Resin-impregnated Wool Filters (X p. 354).

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Viscosities and Solubilities of Synthetic Detergent Mixtures containing Soluble Silicates. R. Getty and N. McCready. *J. Amer. Oil Chem. Soc.*, **30**, 193-196 (May 1953).

Slurries containing synthetic detergents, silicates, phosphates, and sometimes other additives were prepared and their viscosities measured at several stresses. Portions of the mixtures were oven-dried and dilute solutions prepared. Their turbidities and pH values were determined. Mixtures of silicate with pyrophosphate yielded lower viscosities and turbidities than mixtures with tripolyphosphate. A mixture of the two phosphates with silicate resulted in a still lower viscosity, but an intermediate turbidity. Increasing the alkalinity of the silicate decreased the turbidity, but the minimum viscosity occurred at an intermediate silicate ratio in most cases. A number of the additives tested lowered the viscosity, and all lowered the turbidity. P. G. M.

Role of Surface-active Agents in Wetting. F. M. Fowkes. *J. Physical Chem.*, **57**, 98-103 (1953); *Chem. Abs.*, **47**, 4691 (25 May 1953).

The relation between sinking time and wetting agent depends on the extent of adsorption during penetration. For strongly adsorbed substances, e.g. Triton X-100 and Nonic 218, the rate of wetting is affected by the extent of diffusion of the agent from the bulk solution to the surface. Where the wetting agent is not depleted by adsorption, e.g. Aerosol OT and MA, Tergitol 4, the contact angle is the determining factor. Sinking times are related to surface tension by—

$$\log t_s = A + B/\gamma$$

(t_s = sinking time; γ = surface tension, which depends on the concentration and is related to the contact angle). Wetting properties can be correlated with the molecular structure of the wetting agent by knowledge of the critical concentration needed for micelle formation. C. O. C.

PATENTS

Diethylenetriamine—Detergent. M. Rosenfeld and C. F. Pickett. USP 2,616,856

The condensation product of diethylenetriamine and diacetone alcohol enhances the detergent properties of diethylenetriamine. C. O. C.

Size for Synthetic Linear-polymer Yarns. Monsanto. USP 2,616,867

Nylon, acrylic polymer, etc. yarns are sized with a choline salt of the copolymer of an ethylene- α,β -dicarboxylic anhydride or acid or an alkyl (Alk of <4 C) hydrogen ester of such acid and an aromatic compound containing a single >C:CH₃ group. The solution should have pH 4.5-9.5 and preferably be at 130-150°F. The sized yarns have high wearing efficiency and excellent abrasion resistance. C. O. C.

Antistatic Agents for Vinyl Polymers containing no Free Hydroxyl Groups. ICI. BP 692,929

Addition of 2-25% by wt. of a synthetic linear *N*-alkoxymethylpolyamide, e.g. those described in BP 573,482, to vinyl polymers containing no free hydroxyl groups reduces their tendency to accumulate electrostatic charges. C. O. C.

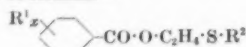
Diesterified Phosphono Derivatives of Esters, Amides, or Nitriles of Propionic Acids—Flame-retardant Plasticisers. Union Carbide & Carbon Corp. BP 693,742

Compounds of formula (R¹O)₂PO-CR²R³-CHR⁴-X (R¹ = sat. aliphatic, alicyclic, or aromatic hydrocarbon radical or alkoxyalkyl, aryloxyalkyl, or cycloalkoxyalkyl; R² = H, Alk, Ar, or alkenyl; R³ and R⁴ = H or Alk;

X = COOR⁵, CO-NR⁶, or CN; R⁵ = Alk, cycloalkyl, alkenyl, aralkyl, alkoxyalkyl, aryloxyalkyl, or cycloalkoxyalkyl; R⁶ = H, Alk, or Ar) are plasticisers for thermoplastic resins and cellulosic derivatives. Where each R¹ = an alkoxyalkyl of >2 C and one O atom in a carbon-to-carbon linkage, or a hydrocarbon residue of >3 C and free from olefinic double bonds, then the products have use as flame-retardant plasticisers. C. O. C.

Plasticisers for Vinyl Chloride Polymers and Copolymers. Monsanto. USP 2,617,778

Compounds of formula—



(R¹ = CH₃ or Cl; R² = hydrocarbon radical of 4-12 C; x = 0-2) are valuable plasticisers for vinyl chloride polymers and copolymers of >70% vinyl chloride content. C. O. C.

Mothproofing (X p. 354).

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

The N-N Stretching Frequency. R. J. W. Le Fèvre, M. F. O'Dwyer, and R. L. Werner. *Chem. and Ind.*, 378 (18 April 1953).

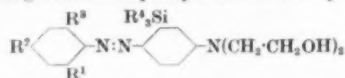
The spectra of thirty-six azo compounds, including diazoates, diazocyanides, diazosulphonates, diazosulphones, azoxysulphones, aromatic 3:3-dimethyltriazene and diazocarbonylamides, 2:2'-azopyridine, 1-methyl-1:2:3-benzotriazole, and azobenzenes, have been examined between 600 and 1800 cm.⁻¹ and show common absorption maxima at ca. 1406 cm.⁻¹ and ca. 1577 cm.⁻¹. It is considered that 1576 cm.⁻¹ is due to N=N stretching. A. J.

Kinetics of the Diazo Coupling Reaction. H. Zollinger. *Chem. Rev.*, **51**, 347-361 (1952); *Chem. Abs.*, **47**, 4856 (25 May 1953).

A review with 43 references. C. O. C.

Silicon-containing Azo Dyes—II. S. V. Sunthakar and H. Gilman. *J. Org. Chem.*, **18**, 47-54 (1953); *Chem. Abs.*, **47**, 6141 (25 June 1953).

Stirring 13 g. *m*-Br-C₆H₄-N(CH₂-CH₂OH)₂ in 75 c.c. ether with 0.15 mole of Li butoxide in 100 c.c. ether at -20°C. for 1 hr. while gradually allowing the temp. to rise to 20°C., stirring for another 15 min., adding 7 g. trimethylsilicon chloride in 50 c.c. ether, stirring for 1 hr., and then pouring into ice-dil. HCl, extracting the ether layer with dil. HCl, making the combined acid soln. alkaline with Na₂CO₃, extracting with ether, and evaporating the ether extract gave 87% of an oil. On washing this oil with petroleum ether (30-40°) and recrystallising from petroleum ether (60-70°), 51.4% of *m*-(CH₃)₂Si-C₆H₄-N(CH₂-CH₂OH)₂ (I) was obtained. Similarly, *m*-(C₂H₅)₂Si-C₆H₄-N(CH₂-CH₂OH)₂ (II) was obtained in 36.5% yield. Addition of a diazotised amine to an ice-cold soln. of I or II, stirring for 30 min., neutralising the mineral acid with Na acetate, and diluting with water precipitated the azo dyes—



of which the following have been prepared—

R ¹	R ²	R ³	R ⁴	Yield (%)	Colour
H	NO ₂	H	C ₆ H ₅	50	Brownish red
Cl	NO ₂	H	C ₆ H ₅	50	Bordeaux
Cl	NO ₂	Cl	C ₆ H ₅	57	Brownish red*
CH ₃ -SO ₂	NO ₂	H	C ₆ H ₅	25	Bluish violet
CH ₃ -SO ₂	CH ₃ -SO ₂	H	C ₆ H ₅	20	Dark red
H	NO ₂	H	CH ₃	50	Brownish red
Cl	NO ₂	H	CH ₃	60	Bluish violet
Cl	NO ₂	Cl	CH ₃	60	Brownish red
CF ₃	NO ₂	H	CH ₃	50	Bluish violet
CH ₃ -SO ₂	NO ₂	H	CH ₃	52	Bluish violet
CH ₃ -SO ₂	CH ₃ -SO ₂	H	CH ₃	34	Brownish red

* This dye was obtained in two forms, of m.p. 169-170°C. and 218°C. respectively, separated by chromatographic fractionation. C. O. C.

Naphthol Dyes and Intermediates. II—Preparation of 3-Methoxy-4-amino-diphenylamine. S. Yura, I. Tanaka, and K. Nakao. *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **54**, 422-424 (1951); **III—Synthesis of Naphthols containing a Hydroaromatic Nucleus.** S. Yura and K. Nakao. *Ibid.*, 424-426; *Chem. Abs.*, **47**, 5121 (25 May 1953).

II— Several attempts to make 3-methoxy-4-amino-diphenylamine from 3-hydroxydiphenylamine are described. The preferred method is to methylate with $(\text{CH}_3)_2\text{SO}_4$, couple the resulting 3-methoxy compound with diazotised sulphanilic acid at the 4-position, and then reduce to sodium hydrosulphite.

III— Azoic coupling components containing a hydroaromatic nucleus have been prepared by condensing 2:3-hydroxynaphthyl chloride with hydroaromatic amines, e.g. cyclohexylamine, or hexahydro-*p*-phenylenediamine. The products have affinity for cotton from alkaline baths and for cellulose acetate from neutral baths. C. O. C.

Dye Phosphors. I—Phosphorescent Bodies suitable for Dye Phosphors. D. Yamamoto. *J. Chem. Soc. Japan, Pure Chem. Sectn.*, **73**, 739-744 (1952); **II—Quenching of the Phosphorescence by Free Water in the Dye-Gelatin Phosphors.** *Ibid.*, 794-796; *Chem. Abs.*, **47**, 3702 (25 April 1953).

I— Trials with various compounds using tryptaflavin as a dye phosphor showed that crystals or high polymers containing COOH, OH, or CO-NH groups are suitable as phosphorescent bodies. In the case of crystals it is necessary that the dye should be soluble in the phosphorescent body. Denatured or coagulated proteins do not lose their function as phosphorescent bodies: presumably polypeptide chains are not destroyed, or acid groups still remain.

II— In the gelatin-, agar-agar-, and gum arabic-tryptaflavin systems the maximum amount of water which did not quench phosphorescence agreed excellently with the amount of bound water. C. O. C.

Franck-Condon Principle in the Spectra of Dye Aggregates. G. Scheibe and V. Zanker. *Z. Physik*, **133**, 244-249 (1952); *Chem. Abs.*, **47**, 4737 (25 May 1953).

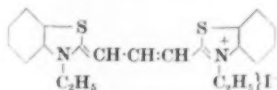
The intensity distribution of the spectral bands of ionic dyes, e.g. Acridine Orange and pentamethincyanine, changes markedly, both in fluorescent emission and in absorption, with change in concentration. Assuming that the equilibrium positions of the molecules both in the ground state and in the excited states are displaced with respect to one another on account of association, then this behaviour can be explained with the help of the Franck-Condon principle. One of the dye bands, at the extreme long-wave side, is phosphorescent (half-life 0.1 sec.), and therefore belongs to a transition from a metastable state. C. O. C.

Cyanine Dyes. H. Zenno. *J. Soc. Sci. Phot. (Japan)*, **14**, 44-49, 96-101 (1951-52); *Chem. Abs.*, **47**, 3733 (25 April 1953).

An account of the preparation of carbocyanine dyes, e.g. 1:1'-dimethyl-2:2'-trimethinquinocyanine 1-iodide, from the corresponding components, e.g. quinaldine methiodide and ethyl orthoformate, and as condensing agents 2-aminothiazole, formanilide, diphenylmethane, or benzyl cyanide. C. O. C.

Formation of Methin Bridges by the Action of Formamide. I—Trimethincyanines. S. Hünig. *Annalen*, **574**, 99-106 (1951); **II—Oxonols.** *Ibid.*, 106-112; **III—merocyanines.** *Ibid.*, 112-121; *Chem. Abs.*, **47**, 3850 (25 April 1953).

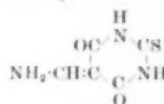
I— Condensation of formamide, preferably at 130°C., for 2 hr. with 3-ethyl-2-methylbenzothiazolium *p*-toluenesulphonate and addition of KI yielded 64% of "thiazole purple"—



In the same way formamide with 1-ethyl-2-methyl-naphtho[1,2]thiazolium *p*-toluenesulphonate in 4 hr. yielded 30% of the dark blue bis[2-(1-ethylnaphthothiazole)]trimethincyanine bromide, and with the 1-ethylquinaldinium

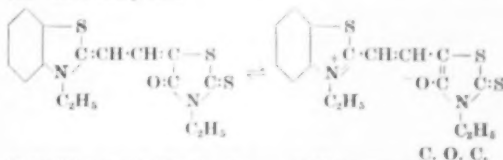
salt yielded in 8 hr. 12% of the green bis[2-(1-ethylquinoline)]trimethincyanine iodide. With 3-ethyl-2-methylbenzoxazolium iodide, 1-ethyl-2:3:3-trimethyl-*p*-indolium iodide, and *N*-alkyl-benzimidazolium and -benzoselenazolium salts, coloured products were not obtained.

II— Compounds in which a CH_2 group is vicinal to and activated by a $>\text{C}=\text{O}$ group yielded at 130°C. with formamide the following methinoxonols—from 3-hydroxythianaphthen (4 hr.) 97% of the reddish-brown bis[2-(3-oxodihydrothianaphthen)]-, from phenylmethyl-5-pyrazolone (1 hr.) 85% of the orange-yellow bis[4-(3-methyl-1-phenyl-5-pyrazolone)]-, from 3-ethylrhodanine (8 hr.) 58% of bis[5-(3-ethylrhodanine)]-, and from the 3-phenyl analogue (2-4 hr.) 56% of the brown bis[5-(3-phenylrhodanine)]-methinoxonol. All of these methinoxonols gave red acidic soln., changing to violet on treatment with Ag^+ , Hg^{2+} , or Cu^{2+} salts followed by pptn. of the corresponding salts. These reactions appear to be very sensitive, and may serve in quantitative analysis. Thiobarbituric acid (0.72 g.) and formamide (1 c.c.) heated for 1 hr. at 130°C. gave 100% of the yellowish compound—



Dimethylformamide and barbituric acid refluxed for 5 hr. gave the dimethylamine salt of bis[5-(barbituric acid)]-methinoxonol, whose deep yellow soln. in NaOH yields the corresponding Na salt with NaCl. Dimethylformamide with thiobarbituric acid yielded the dimethylamine salt of bis[5-(thiobarbituric acid)]methinoxonol, dissolving to an orange soln. in water and NaOH and forming the insol. Na salt with NaCl.

III— Formamide, 3-ethyl-2-methylbenzothiazolium *p*-toluenesulphonate, and the appropriate heterocyclic compounds yielded at 130°C. [2-(3-ethylbenzothiazole)]-dimethinmerocyanines, e.g. from 3-ethylrhodanine (8 hr.) the violet compound—

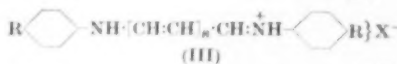
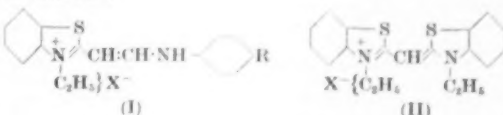


C. O. C.

β -Anilinoethyl Derivatives of Heterocyclic Bases.

III—Syntheses and Absorption Spectra. A. van Dormael and J. Nys. *Bull. Soc. chim. Belg.*, **61**, 614-621 (Dec. 1952).

The quaternary ammonium salts of substituted anilino-vinylbenzothiazoles (I: $\text{R} = \text{NO}_2$, COOH , COOC_2H_5 , CO-CH_3) have been prepared and their optical properties compared with those of the methinbenzothiazole compound (II) and the corresponding "anilinoacrolein anils" (γ -anilinoallylenemines—III: $n = 1$). The optical properties of these anils (III), which could not be prepared, were deduced from those of the pentamethin anils (III: $n = 2$). Substitution of these electrophilic groups in the molecule had a bathochromic effect, the observed λ_{max} being greater than the calculated λ_{max} in each case.



C. H. R.

Synthesis of mesoMethyltrimethincyanine Dyes from NN'-Diphenylacetamidine. Y. Hishiki.

Rept. Sci. Research Inst. (Japan), **28**, 250-256 (1952); *Chem. Abs.*, **47**, 4771 (25 May 1953).

Quaternary methylegdoammonium salts have been condensed with $\text{CH}_3\text{C}(\text{N-C}_6\text{H}_5)_2\text{NH-C}_6\text{H}_5$ (2:1 mol.)

(obtained as a by-product in the preparation of 2-methylbenzothiazole from acetanilide with P_2S_5) in a pyridine base to yield mesomethyltrimethincyanine dyes. Thus 2-methylbenzothiazole methiodide heated with $CH_3C(NC_6H_5)NH-C_6H_5$ in 2-picoline at 150–160°C. for a few min. yielded 1:1':8-trimethyl-2:2'-trimethinthia-cyanine iodide. Various similar syntheses are given. Stronger basicity of the condensing agent gave higher yields, with a maximum at the dissociation constant 1×10^{-8} .

C. O. C.

Naphthenone Sensitisers. I—Polymethinoxonol Dyes and their Intermediates. T. Ogata, R. Tanno, and K. Nishida. *Rept. Sci. Research Inst. (Japan)*, **28**, 259–263 (1952); *Chem. Abs.*, **47**, 5284 (10 June 1953).

The synthesis is described of—

- 4-Anilino-methin-3-methyl-1-phenyl-5-pyrazolone
- 3:3'-Dimethyl-1:1'-diphenylmonomethinpyrazolone
- 4-Phenylaminopentadienyl-3-methyl-1-phenyl-5-pyrazolone
- 3:3'-Dimethyl-1:1'-diphenylpentamethinpyrazolocyanine
- 5-Anilino-methin-3-phenylrhodanine
- 3:3'-Diphenylmonomethinrhodaninecyanine
- p-Methyl-a-cyano-a-anilino-methinacetophenone
- pp'-Dimethylcyanomonomethinacyanoacetophenonecyanine
- p-Methyl-a-cyano-a-anilino-pentamethinacetophenone
- pp'-Dimethylcyanopentamethinacyanoacetophenonecyanine.

C. O. C.

Interpretation of the Absorption Spectra of Certain Classes of Organic Dyes. S. Nikitine. *Gazz. Chim. ital.*, **82**, 476–482 (1952); *Chem. Abs.*, **47**, 4738 (25 May 1953).

By means of the theory of the metal model (cf. Bayliss, *Chem. Abs.*, **42**, 4058 (1948); Kuhn, *ibid.*, **43**, 1653 (1949) and **44**, 433 (1950)) and approximation methods described in earlier work, the positions of the absorption bands and the intensities of these bands were calculated for Methylene Blue and Thionine. Agreement between theory and experimental results was good with Methylene Blue, but not so good with Thionine. The discrepancy with the latter is probably not attributable to a fault in the theory but to an error in calculating the extinction coefficient because of incorrect concentration.

C. O. C.

Polycyclic Aromatic Hydrocarbons as Starting Materials for the Synthesis of Dyes. T. Holbro. *J. Appl. Chem.*, **3**, 1–9 (Jan. 1953).

Phthaloyl Hydrocarbons.—Disubstituting pyrene and fluoranthene with phthaloyl gave the mixtures I and II, which were new yellow vat dyes. With pyrenoline a red vat dye (III) was obtained.

Vatiable Quinones.—The preparation of vat dyes by reaction of halogen derivatives of the quinones of pyrene, chrysene, and fluoranthene with aromatic amines met with little success. 4:5:9:10-Tetrachloro-3:8-pyrenequinone (IV), obtained by chlorinating the quinone, gave with aromatic amines olive green dyes. 2:5:7:10-Tetrachloro-3:8-pyrenequinone (V), from the oxidation of hexachloropyrene, gave with aniline the parent dye (VI) of Anthrasol Green I3G (IG).

Anthrimides.—2:8-Dibromochrysene with 1-amino-4-benzamidoanthraquinone gave an unvatiable blue pigment (VII: dotted bonds omitted), which with conc. H_2SO_4 gave the corresponding carbazole (VIII), a red-brown vat dye. Similarly, 3:8-dibromofluoranthene with 3-amino-1:2-phthaloyl-5-acridone gave a green vat dye (VIII: dotted bonds omitted), which with conc. H_2SO_4 was converted to a grey carbazole vat dye (VIII). Yellow-brown to black-brown dyes having very good fastness properties have been prepared from dihalogenophthaloyl hydrocarbons, an example being the olive-brown vat dye IX.

Acylaminanthraquinones and Related Azoles.—Yellow dyes of high tinctorial strength were obtained from fluoranthene-3:8-dicarboxylic chloride and vatiable amines, e.g. X. The acyl chloride itself was obtained from the dihalogenofluoranthene via the dinitrile (with cuprous cyanide), which was hydrolysed. With aminoanthraquinones substituted *ortho* to the amino group, the corresponding iminazole (e.g. XI: Z = NH), oxazole (e.g. XII), and thiazole (e.g. XI: Z = S) dyes were obtained.

Anthraquinone-Acridones.—The best results were obtained from pyrene. The "anthraquinone-pyrene-acridone" XIII is a green dye, whereas the corresponding "anthraquinone-benzacridone" (phthaloylacridone) is a red-violet.

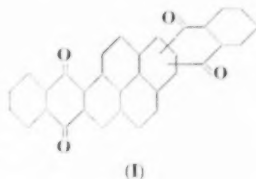
Wool Dyes.—The reaction of amines of pyrene and chrysene and of their sulphonic acids with 1-amino-4-bromoanthraquinone-2-sulphonic acid gave acid wool dyes (e.g. XIV and XV).

Sulphur Dyes.—The introduction of sulphur into various polycyclic hydrocarbons and their quinones gave sulphur dyes having no particularly valuable properties.

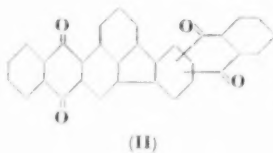
Azo Dyes.—Polyazo dyes of high substantivity and good fastness properties have been made from the amines of pyrene and chrysene and their sulphonic acids. Good results were obtained from the 2-hydroxy-3-naphtho-N-pyrenylamides (e.g. XVI).

Other polycyclic compounds, such as fluorene, phenanthrene, triphenylene, perylene, picene, dinaphthoperylene, rubicene, perflanthene, decacycene, and α - and β -truxene, have also been examined.

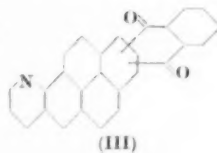
The introduction of polycyclic hydrocarbon nuclei into dye molecules has a positive influence on tinctorial strength and fastness properties, especially with disubstituted fluoranthene derivatives, where the positions of the substituents are comparable with those in *pp'*-derivatives of diphenyl. Thus with the three red dyes XVII, of similar colour, the tinctorial strength increases with increase in the number of rings. Similarly, with the brown carbazole dyes XVIII, the light fastness increases with increase in the number of rings.



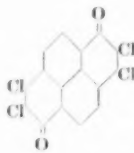
(I)



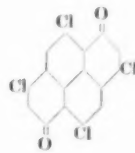
(II)



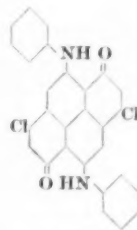
(III)



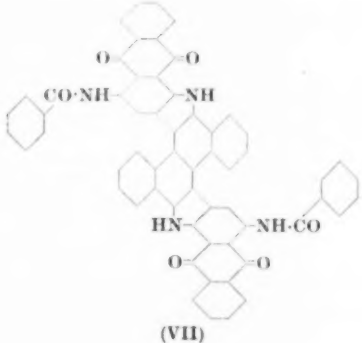
(IV)



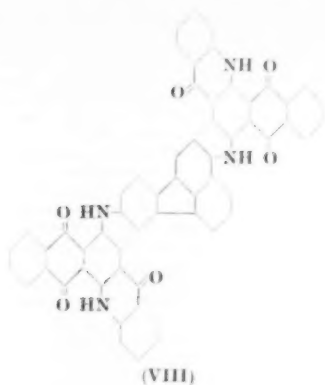
(V)



(VI)



(VII)

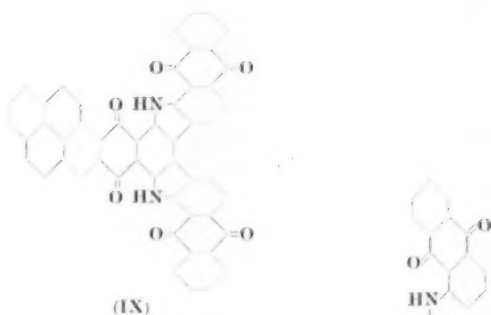


(VIII)

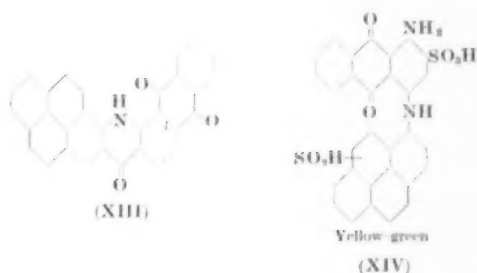


Yellow brown

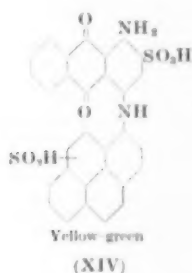
(XII)



(IX)

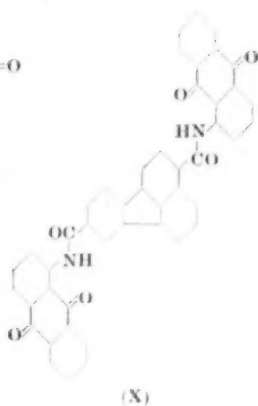


(XIII)

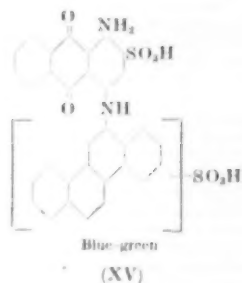


Yellow-green

(XIV)

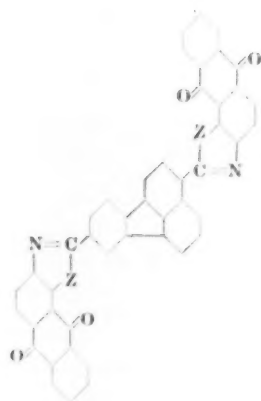


(X)



Blue-green

(XV)



Z = NH: Orange-brown

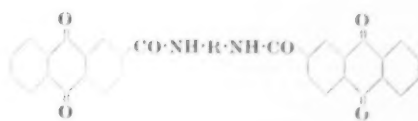
Z = S: Yellow-brown

(XI)



Bluish violet

(XVI)



(XVII)



C. H. R.

Acenaphthene Vat Dyes. I—Synthesis of Naphthalimide and Indanthren Red GG. T. Maki and S. Hashimoto, *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **54**, 479-481 (1951); *Chem. Abs.*, **47**, 5685 (10 June 1953).

Acenaphthene was oxidised in glacial acetic acid with 2.5 mol. of $\text{Na}_2\text{Cr}_2\text{O}_7$ to acenaphthenequinone, then with 0.67 mol. of $\text{Na}_2\text{Cr}_2\text{O}_7$ to naphthalic acid (yield 84.1%). The acid was heated with HNO_3 (sp. gr. 1.40) to give 97.5% yield of the anhydride. Naphthalimide was produced in 97.9% yield when naphthalic anhydride was heated in 10% aq. ammonia (3 moles of ammonia) for 5 hr. Fusion of naphthalimide with 70% KOH at 240°C. for 30 min. gave perylenetetracarboxydimide (82.6%). NN' -Dimethylation by boiling the dry disodio derivative with 2.5 mol. of methyl *p*-toluenesulphonate and 0.62 mol. of Na_2CO_3 in *o*-dichlorobenzene for 6 hr. resulted in a 93.3% yield of a product identical with Indanthren Red GG (IG). C. O. C.

Acenaphthene Vat Dyes. II—Amine Condensation of Perylenetetracarboxylic Anhydride and Constitution of Indanthren Scarlet R. T. Maki and S. Hashimoto, *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **54**, 544-546 (1951); *Chem. Abs.*, **47**, 6143 (25 June 1953).

Scarlet R (principal constituent of Indanthren Scarlet R (IG)) was obtained in 96.6% yield by heating 1 mol. of perylenetetracarboxylic anhydride with 16 mol. of anisidine at 215°C. for 5 hr. and then treating with 10% aq. HCl and 1% aq. NaOH. Its constitution is NN' -bis-*p*-methoxyphenylperylene-tetracarboxydimide. Similar vat dyes, e.g. NN' -bis-*o*-methoxy-, *p*-ethoxy-, *p*-methyl-, *p*-chloro-, *p*-1-anthraquinonylamino-, and *p*-2-anthraquinonylamino-phenylperylene-tetracarboxydimide and the NN' -diphenyl analogue were prepared in the same way. All dyed cotton red except the *o*-methoxy derivative, which gave a violet. C. O. C.

Electronic Structure of Heterocyclic Compounds with an Intranuclear -CO-NH- Function. E. Riesz, *Rev. Facultad Humanidad y Cienc., Univ. Montevideo*, **117** 122 (1952); *Chem. Abs.*, **47**, 2490 (10 March 1953).

A survey has shown that oxindole exists in the carbonyl rather than in either of the hydroxy forms. Oxindole (I) prepared from isatin (II) by Murschalk's method (*Chem. Abs.*, **6**, 1436 (1911)) contains isatide, I (1 part) and benzoic anhydride heated at 150-160°C. for 1-1.5 hr., extracted free from I with dilute base, and crystallised from petroleum ether gave 1-benzoyloxindole (III). 1-Benzoyl-isatin (IV) was prepared by Callow and Hope's method (*Chem. Abs.*, **23**, 4469 (1928)), in acetic acid with benzoic anhydride. Acetic acid solutions of III and slight excess of diazotised 2:4-dichloroaniline after three days in the dark gave a theoretical yield of the yellow dye 3-(2:4-dichlorophenylazo)-1-benzoyloxindole. The same dye was obtained also from equimolecular proportions of IV and 2:4-dichlorophenylhydrazine in boiling acetic acid. Similarly, diazotised *p*-aminobenzenesulphonic acid and *p*-phenylhydrazinesulphonic acid gave with III and IV respectively *p*-(1-benzoyl-3-oxindolylazo)benzenesulphonic acid, a

similar dye being obtained with I and II respectively. Both are yellow dyes for silk and wool, the corresponding dye from indoxyl being orange. C. O. C.

Fluorescent Brightening Agents. I—Quantitative Determination of Dyeing Characteristics. A. Yabe, *Nat. Sci. Rept. Ochanomizu Univ.* (Tokyo), **2**, 142-147 (1951); *Chem. Abs.*, **47**, 5121 (25 May 1953).

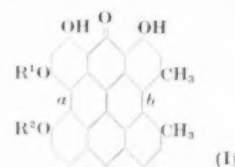
The fluorescence of 4:4'-bis(4-amino-*s*-triazinyl-2-amino)-2:2'-stilbenedisulphonic acid derivatives on starch-free bleached calico or in solution (measured with a Pulfrich photometer and a Duboscq colorimeter) increased with concentration to a maximum and then decreased, showing the so-called concentration quenching. The intensity q was related to the concentration c by $q = k_1 c$ ($k_1 = \text{constant}$) up to c_0 , the concentration giving maximum intensity (ca. 0.3% on cotton), but beyond this point the relation was $\log q_0/q = k_2 c$ ($q_0 = \text{intensity at } c_0$; $k_2 = \text{constant}$). The relative brightness of the treated cloth was 2% greater than that of the untreated cloth in direct sunlight, but only 0.3% greater under a 100-w. lamp. The varying amount of ultraviolet radiation present under practical testing conditions makes results unreliable. Addition of soap or neutral salts sensitises the fluorescence. C. O. C.

Synthesis of Lawsone. A. C. Jain and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **35A**, 233-241 (1952); *Chem. Abs.*, **47**, 3287 (10 April 1953).

4-Methoxy-1-naphthol (I) (5 g.) is refluxed for 6 hr. with hexamethylenetetramine in acetic acid, boiling conc. HCl added, and the mixture heated for 10 min. longer on the steam-bath and left overnight in a refrigerator, yielding 1-hydroxy-4-methoxy-2-naphthaldehyde (II), also obtained from I and HCN in ether in presence of ZnCl_2 . II with 5% H_2O_2 in 4% aq. NaOH and pyridine gives a 50% yield of lawsone (2-hydroxy-1:4-naphthoquinone). Peroxysulphate oxidation of 2-acetyl-1-naphthol gives a 50-60% yield of lawsone. Partial methylation of 2-acetyl-1:4-naphthalenediol gives 2-acetyl-4-methoxy-1-naphthol, which on oxidation gives a 35-40% yield of lawsone. C. O. C.

Protogapopyrine and Fagopyrine, the Photodynamic Pigments of Buckwheat, *Fagopyrum esculentum*. H. Brockmann, E. Weber, and G. Pampus, *Annalen*, **575**, 53-83 (1951); *Chem. Abs.*, **47**, 3841 (25 April 1953).

A large part of the pigment from buckwheat flowers, formerly considered to be fagopyrine, is actually a light-sensitive progenitor—protogapopyrine—which on irradiation is converted into the far less soluble fagopyrine (I). (R^1 and $\text{R}^2 = \text{undetermined groups included in } \text{C}_{14}\text{H}_{22}\text{O}_2\text{N}_2$). In protogapopyrine either bond (a) or bond (b) is broken.



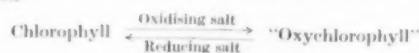
C. O. C.

Dyeing Constituents in "Yama-Kariyasu". II—Colour-developing Action of Ash from Camellia Leaves on the Dyeing Constituents. M. Miyoshi, *J. Chem. Soc. Japan, Pure Chem. Sectn.*, **73**, 857-859 (1952); *Chem. Abs.*, **47**, 6145 (25 June 1953).

Silk is dyed a golden yellow by first treating it with an aqueous extract of yama-kariyasu and then developing with the ash of camellia leaves, the optimum pH of the developing liquor being 9.6-10.0. Development is caused principally by the Ca and the K in the ash. C. O. C.

Reversible Bleaching of Chlorophyll by Metallic Salts. W. F. Watson, *J. Amer. Chem. Soc.*, **75**, 2522 (20 May 1953).

Confirmation has been obtained that the reversible action—



does occur. Reversion of the straw-coloured "oxychlorophyll" to green on addition of NaCl or on exposure to air

is not regeneration of chlorophyll but formation of allomerised chlorophyll. The reversion of colour caused by quinol is due to production of yet another green compound.

C. O. C.

Orientation in the isoFlavone Series. W. Baker, I. Dunstan, J. B. Harborne, W. D. Ollis, and R. Winter. *Chem. and Ind.*, 277 (21 March 1953).

Demethylation of 5:7-dihydroxy-8:3':4':5'-tetramethoxyisoflavone with hydrobromic and acetic acids gives 5:6:7:3':4':5'-hexahydroxyisoflavone. In some cases synthesis of isoflavones by the ethyl formate method gives compounds with 5:6:7 orientation, whereas the ethoxalylolation process gives 5:7:8 orientation.

C. H. R.

Isomerisation of isoFlavones. W. B. Whalley. *Chem. and Ind.*, 277-278 (21 March 1953).

Demethylation of 5:7:2'-trimethoxy-8-methylisoflavone (I) with aluminium chloride in benzene and with hydriodic acid containing acids derived from phosphorus gave a mixture of 5:7:2'-trihydroxy-8-(and 6)-methylisoflavone. Remethylation of this mixture gave the parent isoflavone (I) and the corresponding 5:7:2'-trimethoxy-6-methylisoflavone (II), the structure of which was proved by alkali degradation. 5:7:2'-Trihydroxyisoflavone with methyl iodide in sodium methoxide gave 5-hydroxy-7:2'-dimethoxy-6-methylisoflavone, which on further methylation gave II. The demethylation of 5:7:4'-trimethoxy-8-methylisoflavone with hydriodic acid gave the corresponding trihydroxy derivative together with a little of the isomeric 5:7:4'-trihydroxy-6-methylisoflavone. C. H. R.

Identification of Leuco Anthocyanins as "Tannins" in Foods. E. C. Bate-Smith and J. Svain. *Chem. and Ind.*, 377-378 (18 April 1953).

It is suggested that the red-brown ppt. produced by boiling "condensed" tannins with mineral acid (phlobaphen test), and generally ascribed to catechins, is probably due to leuco anthocyanins. Leuco anthocyanins from *Pinus maritima* and cacao beans yield cyanidins and a red-brown ppt. on being heated with dil. HCl, and give a positive vanillin reaction, whilst catechins give greyish-brown ppt. with dil. HCl.

A. J.

Alkyl Shifts in Absorption Spectra of Azulene and other Aromatic Molecules. C. A. Coulson. *Proc. Phys. Soc.*, 65A, 933-945 (1952); *Chem. Abs.*, 47, 3694 (25 April 1953).

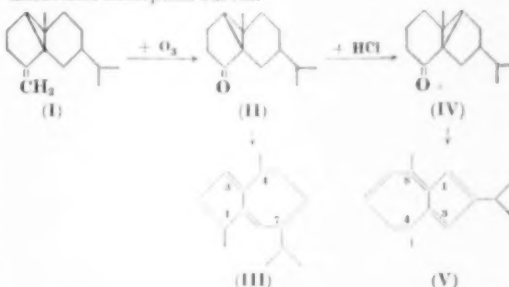
An enquiry into the factors which cause shifts in the ultraviolet spectra of aromatic molecules on substitution. The method of molecular orbitals is used and discussion is confined to π -electrons. There are two main effects—(a) electrostatic or inductive and (b) conjugative or mesomeric. In alternant hydrocarbons (b) predominates and causes a red shift. In other molecules, e.g. azulene and quinoline, (a) is considerably larger and predominates over (b). Different positions of substitution lead sometimes to red shifts and sometimes to blue shifts. Electron donors cause shifts in opposite directions to electron acceptors. Calculations are given of spectral shifts for ethylene, benzene, naphthalene, anthracene, and benzanthracene. Normal alkyl shifts in the long wave band are to the red because of greater delocalisation of the π -electrons. In alternant hydrocarbons the delocalisation effect seems to be greater than the electrostatic effect. This by itself would cause blue shifts. But in other molecules, including both non-alternant hydrocarbons, e.g. azulene, and heteronuclear molecules, e.g. quinoline, the electrostatic effect is several times larger than before and dominates the phenomenon. The shifts due to two or more substituents are additive. This appears satisfactory for alternants. The successive shifts in the series benzene \rightarrow toluene \rightarrow *p*-xylene are 78 and 75 Å, respectively. In the methylazulenes a slightly less strict additivity obtains.

C. O. C.

Azulenes. W. Treibs and H. Barchet. *Forschungen und Fortsch.*, 24, 4 (1948); *Chem. Zentr.* (Russian Zone edition), 1, 1125 (1949); *Chem. Abs.*, 47, 4312 (10 May 1953).

The tricyclic compound aromadendrene $C_{15}H_{24}$ (I) is obtained from *Eucalyptus globules* (cf. Radcliffe and Shut, *Chem. Abs.*, 32, 8397 (1938)). With ozone it yielded apoaromadendrone $C_{15}H_{20}$ (II), which with CH_3MgI gave the corresponding methylcarbinol; splitting off water and dehydrogenation yielded blue guaiazulene $C_{15}H_{18}$ (III). In presence of HCl II was spontaneously converted into

iso-apoaromadendrone (IV). By the above procedure IV was converted into the red vetivazulene (V). The "angular" CH_3 group is responsible for the transition from II to IV. Slight amounts of the azulene parent substance can be produced by the action of acetylene on Cu alloys. Some bicyclic and tricyclic azulenes give the same fundamental ultraviolet absorption curves.



C. O. C.

Terpenes. XXV Complete Synthesis of S-Guai-azulene. F. Šorm, J. Gut, J. Hlavnička, J. Kučera, and L. Sedivý. *Collection Czechoslov. Chem. Commun.*, 16, 168-183 (1951); **XXVI—Complete Synthesis of Se-Guaiazulene.** F. Šorm, J. Kučera, and J. Gut. *Ibid.*, 184-197; *Chem. Abs.*, 47, 4313 (10 May 1953).

XXV—The bright blue S-guaiazulene has been synthesised starting from 3:4-dimethoxybenzaldehyde and shown to be 1:4-dimethyl-7-isopropylazulene [(III), previous abstract].

XXVI—Dehydration of guaiene [guaiene (?)] yields two isomeric azulenes depending on the temperature and/or dehydrogenating agent. Thus at lower temperatures with S, bright blue S-guaiazulene is formed; and at higher temperatures with Se or S, the violet Se-guaiazulene results. The latter has been synthesised, and shown to be 2:4-dimethyl-7-isopropylazulene.

C. O. C.

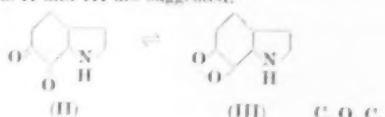
Anthochlor Pigments of *Cosmos sulphureus*, *Coreopsis lanceolata*, and *C. saxicola*. M. Shimokoriyama and S. Hattori. *J. Amer. Chem. Soc.*, 75, 1900-1904 (20 April 1953).

A new anthochlor glycoside—sulphurein—has been isolated from the ray flowers of *Cosmos sulphureus*, and its constitution has been established as the 6-glucoside of sulphuretin (3':4':6-trihydroxybenzylidenecoumaranone). Coreopsin was isolated from the same plant, and its constitution established as the 4'-glucoside of butein (3:4:2':4'-tetrahydroxychalcone). A new chalcone glucoside—lanceolin—has been isolated from *Coreopsis lanceolata* and *C. saxicola*; it is probably the 4'-glucoside of lanceoletin (2':4':3:4-tetrahydroxy-3'-methoxychalcone). Leptosin, the 6-glucoside of leptosidin (3':4':6-trihydroxy-7-methoxybenzylidenecoumaranone) has also been isolated from these two plants.

C. O. C.

Intermediates in the Conversion of 3:4-Dihydroxy-phenylalanine into a Red Pigment. M. Rangier. *Compt. rend. Acad. Sci. Paris*, 234, 2652-2654 (1952); *Chem. Abs.*, 47, 5929 (25 June 1953).

3:4-Dihydroxyphenylalanine (I) under conditions similar to the adrenochrome reaction is converted into a red pigment which does not fluoresce under ultraviolet radiation. Thus, when a pinch of PbO_2 is shaken with 10 c.c. of an acetic acid solution of I (1:10,000, pH 6.5) at 0°C. and the mixture quickly centrifuged, a dark red liquid (II) forms, which spontaneously deposits a dark red pigment (melanin). II is decolorised by adding a drop of conc. aq. $NaHSO_3$, is pptd. by $PbSO_4$, and on centrifuging yields a colourless liquid (III), which has a stable, intense yellow fluorescence under ultraviolet radiation. III gives reactions indicating the presence of a peroxide. The constitutions II and III are suggested.



C. O. C.

Zinc Oxides from the Harz. F. Munk. *Dtsch. Farben-Z.*, 7, 44-48 (1953); *Chem. Abs.*, 47, 5644 (10 June 1953).

The ancient Rammelsberg mines in the Harz mountains contain ores of composition Zn 17-20%, Pb 8-10%, Fe 9-10%, Cu 1%, S 24%, BaSO₄ 25%, and small amounts of Sb, Cd, Ag, and Au. Flotation of the crushed ore yields, among others, concentrates of Zn (44% Zn, 7% Cu), Pb-Cu (35% Pb, 17-18% Zn), and BaSO₄. The Zn concentrate is smelted with coal, leaving an ash containing Zn 9, Pb 6, and C 30%. The Pb-Cu concentrate is roasted, leaving a slag with 17% Zn (probably as ZnO, Fe₂O₃) and 2% Pb. From these by-products and from the large slag heaps (20% Zn) of the ancient Pb works, Zn and Pb are produced by reduction with coal in the Hellwig furnace, followed by oxidation of the vaporized Zn and Pb. The ZnO smoke is precipitated by chilling it rapidly from 1000 to 300°C. The particle size of the ZnO depends on the speed of chilling and on the solids content of the flue gas (about 20 g./cu.m.). Rapid chilling also keeps the ZnSO₄ content of the ZnO low. The product is a co-fumed leaded ZnO. It is obtained as 90% ZnO-5-6% Pb, or as 70% ZnO-20% Pb, and with up to 35% Pb. Impurities are 0.5-1.0% ZnCl₂ or ZnSO₄ and traces of Fe, Cu, Mn, and Cd. The reactivity, toxicity, stability, and particle size of the pigments are discussed. C. O. C.

Optical Properties of Titanium Dioxide. T. Radhakrishnan. *Proc. Indian Acad. Sci.*, 35A, 117-125 (1952); *Chem. Abs.*, 47, 2587 (25 March 1953).

Dispersion formulae are given for the three polymorphic forms of TiO₂ as being of the form—

$$n^2 - 1 = a + \frac{b\lambda^2}{\lambda^2 - \lambda_0^2} - c\lambda^2$$

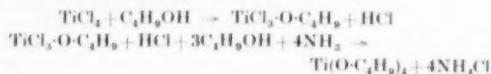
($\lambda_0 = 0.2870 \mu$, for all three modifications; a , b , and c are—

	Index	a	b	c
ANATASE	n	2.4485	2.3998	0.10
	ϵ	2.8325	1.8492	0.18
RUTILE	n	2.2868	2.7275	0.10
	ϵ	2.6034	3.7199	0.20
BROOKITE	n	2.9858	2.1036	0.18
	β	2.6957	2.3130	0.16
	γ	2.4285	2.9641	0.05

The formula gives results correct to the third decimal place. A characteristic frequency at 2870 Å. is present in all cases. The values of dn/dt in the three crystals are explained by large transfers of transition probability and moderate shifts toward longer wavelengths of this frequency as the temperature is raised. Calculations of n and of the refringence of rutile based on the Bragg theory are in good agreement with observed data. C. O. C.

Organic Compounds of Titanium. A. Thomas. *Peintures, Pigments, Vernis*, 28, 457-462 (1952); *Chem. Abs.*, 47, 4102 (25 April 1953).

Organic esters of Ti, especially polymeric butyl titanate, are used in the formulation of Zn-pigmented paints, thin layers of which, covered finally with an Al layer, can withstand temps. of 700°C. for a long time—



Butyl orthotitanate polymerises at 200-250°C., splitting off C₄H₉OH and butene; the polymer contains 65-4% TiO₂, while the monomer contains (theoretically) 23-53%. Complex salts of Ti and various organic acids can be used as pigments. Basic Ti salicylate is yellow, and soluble in alkalis and alkali-metal carbonates. Introduction of other chromophores, e.g. CH=N by condensing methylenedianthranilic acid with 2 mol. of benzaldehyde or dimethylaminobenzaldehyde and precipitating as the Na salts on Ti [sic], yields an ochre or a red pigment respectively. C. O. C.

Molybdenum Blue—II. O. Glemser and G. Lutz. *Z. anorg. allgem. Chem.*, 264, 17-33 (1951); *Chem. Abs.*, 47, 3165 (10 April 1953).

Electrolysis of melts of Na₂O.5-20MoO₃ for 2 hr. at 750°C. (4 v. and 1 amp./sq.cm.) with Mo electrodes yields

a grey product, which after washing with water and ammonia leaves dark violet Mo₂O₁₁. Reduction of a suspension of MoO₃ in 2N-HCl by Zn, Sn, Mo, Al, Fe, KI, SnCl₂, or Na₂S₂O₄ yields steel-blue Mo₂O₁₀(OH)₂ (I), insoluble in water, ammonia, and alkalis. On isobaric decomposition it loses water discontinuously at 230-240°C., yielding a mixture of MoO₂ and MoO₃. When I is exposed to air for 4 years or, after being suspended in water, to a current of air for 14 days, the residue corresponds to MoO_{2.9} but its X-ray pattern is still that of I. The conductivity of I is 10 ohm⁻¹cm.⁻¹; that of the 4-year oxidation product is 3 times as high. Reduction of MoO₃ suspended in conc. HCl with excess Zn, Sn, Ni, or Fe yields the claret MoO_{2.3}, which when dried over conc. H₂SO₄ is air-oxidised to the blue Mo₂O₄(OH)₂ (II). II is insoluble in alkalis and loses water discontinuously between 225 and 235°C. It decomposes at 380°C. to a mixture of MoO₂ and MoO₃. Air oxidation of II for 3 hr. or drying over P₂O₅ for 4 weeks forms I. I can be reduced to II, but stopping at the right point is difficult. The products obtained by heating mixtures of Mo, MoO₃, and a little water in a sealed evacuated tube at 110°C. for 4 weeks depend on the composition of the initial mixture—above MoO_{2.9} no reaction, with MoO_{2.75-2.9} I is formed, and below MoO_{2.75} I and Mo result; no II is formed. Heating any of these mixtures at 150°C. and attempts to hydrate Mo₂O₁₁ by such a method yield only MoO₂ and MoO₃. Similar heating at 110°C. for several weeks of mixtures of MoO₃.2H₂O and Mo with the overall composition MoO_{2.9-2.8} forms Mo₂O₁₀(OH)₂ (III); with the composition MoO_{2.9-2.8} III, MoO₂, and MoO₃ are formed. Aq. ammonia and NaOH have little effect on the product from mixtures of composition MoO_{2.9-2.8}, but the product from the MoO_{2.9} mixture is converted to a yellowish-brown precipitate. III is stable in air, but it loses water discontinuously between 115 and 120°C., leaving MoO₂ and MoO₃. Complete loss of water occurs at 400°C. and Mo₂O₁₁ is left. Treatment of a suspension of MoO₃.2H₂O in dil. HCl with SnCl₂, Sn, or Zn for 14 days yields MoO_{2.6}.rH₂O, which is decomposed by alkali to Mo(OH). Treating MoO₃ with coal-gas by the blowpipe technique forms small amounts of an intensely blue substance having an X-ray pattern different from those of known molybdenum blue compounds. Prolonged treatment with a reducing flame yields dove-blue Mo₂O₂₃. All molybdenum blues precipitated from solution appear amorphous under X-rays even after 4 years and become colloidal in water. With either aq. NaOH or ammonia they are converted to reddish-brown Mo(OH)₃. C. O. C.

Synthetic Iron Oxide Pigments. C. C. Dewitt, A. D. Livingood, M. D. Livingood, and K. G. Miller. *Mech. Eng. Expt. Sta. Bull.* No. 110, 5-50 (1952); *Chem. Abs.*, 47, 5695 (10 June 1953).

An account of the methods and equipment used in producing iron oxide pigments by batch and continuous operations. For black, brown, and red pigments a ferric salt is treated with alkali over the pH range 6-13.5 at 270-325°F. Microscopic examination indicated that the α-Fe₂O₃ (goethite) is in the particle size range 1.5 μ, and smaller. Yellow to orange pigments can be produced by air oxidation of ferrous salts at 68-160°F. A critical survey of the field is given. C. O. C.

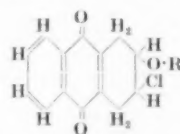
PATENTS

Chlorohydrin Derivatives of Dihydroanthraquinone.

American Cyanamid Co.

USP 2,616,901

Compounds of formula—



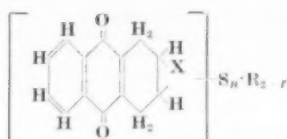
(R = H or a radical of a fatty acid of 2-12 C) are produced by treating 1:4-dihydroanthraquinone with Cl₂ or Br₂ in presence of a hydroxyl compound, e.g. water or a carboxylic acid. They are useful as dye intermediates. C. O. C.

Sulphur Halide Derivatives of Dihydroanthraquinone.

American Cyanamid Co.

USP 2,616,902

Compounds of formula—



(x and $n = 1$ or 2 ; $X = \text{Cl}$ or Br ; $R =$ an aromatic radical), useful as dye intermediates, are produced by treating 1:4-dihydroanthraquinone, preferably dispersed or dissolved in an inert organic liquid, with sulphur halides.

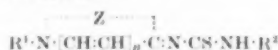
C. O. C.

Substituted Thioureas as Dye Intermediates. General Aniline.

BP 693,310

USP 2,616,894

Compounds of formula—



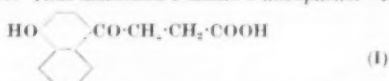
($R^1 =$ subst. or unsubst. Alk, aralkyl, or Ar; $R^2 =$ Alk, Ar, or aralkyl; $n = 0$ or 1 ; $Z =$ atoms to complete a ring of the type used in cyanine dyes) are intermediates for cyanine dyes. They are produced by heating a cycloammonium quaternary salt having a reactive amino group in the α - or γ -position to the quaternary N atom with an alkyl or aryl isothiocyanate in presence of a basic condensing agent.

C. O. C.

Metallisable Monoazo Dyes from β -(4-Hydroxy-1-naphthyl)propionic Acid. Ciba.

BP 693,757

Succinic anhydride or acid chloride reacts with α -naphthol in presence of e.g. AlCl_3 to yield β -(4-hydroxy-1-naphthyl)propionic acid (I), which may also be made by heating alkyl ethers of I with alkali-metal hydroxides, e.g. with 30% aq. NaOH at 130–160°C. I couples with diazotised *o*-aminophenols or *o*-aminonaphthols to give dyes which may be metallised in substance, in the dyebath, or on the fibre. Thus diazotised 2-amino-5-nitrophenol \rightarrow I



dyes wool bordeaux, which becomes violet-brown on after-chroming and violet on aftercoppering.

E. S.

Disazo Dyes. B. Gaspar and P. D. Dreyfuss.

USP 2,612,448

Dyes of formula $A^1-N=N-B-N=N-A^2$ (A^1 and $A^2 =$ azo coupling components having in the 2- or 4-position to the azo group a hydroxy, amino, monoalkylamino, or acylamino radical; $B =$ a subst. or unsubst. aromatic residue bearing the azo groups in the 1:4 position) are exceptionally bright and of great brilliance of hue. Their absorption curves have a very steep increment. They dye gelatin cyan, blue, violet, or magenta of great clarity and excellent fastness, and bleach readily in presence of agents which form reducing agents in presence of metallic silver. They owe their suitability for use in colour photography to the presence of the resonance system—



(m and $n = 1$ or 2 ; Y^1 and $Y^2 = \text{OH}$, NH_2 , NHAlk , or NHAr). C. O. C.

Metal(Chromium or Cobalt)-complex Azo Dyes for Wool, Nylon, etc. Ciba.

BP 693,245

Metal-complex dyes which dye animal fibres, nylon, etc. from an acetic acid bath are made by combining 1 atom of Cr or Co with 1 mol. each of two different *oo'*-dihydroxymonoazo compounds or with 1 mol. of an *oo'*-dihydroxymonoazo compound and 1 mol. of an *oo'*-aminohydroxymonoazo compound, one of the monoazo compounds containing no group imparting water-solubility, and the other containing a sulphonamyl group but no other group imparting water-solubility. Thus, all parts being by weight, the Na salts of the monoazo compounds 2-amino-phenol-4-sulphonamide \rightarrow β -naphthol (3-65) and 2-amino-5-nitrophenol \rightarrow β -naphthol (3-31) are boiled with an aqueous soln. (25) of potassium sodium chromisulphate (having a Cr content of 2-6%) and sulphonated castor oil (6) for 3 hr. The product obtained by salting out dyes wool navy blue from an acetic acid bath.

E. S.

Red Monoazo Pigment. FBv.

BP 689,761

The monoazo compound obtained by diazotising *p*-nitrophenyl 2-aminoanisole-4-sulphonate and coupling with 2-hydroxy-3-naphtho-*o*-toluidide is a vivid red pigment of good fastness to lacquer solvents. The coupling is carried out in presence of mineral acid, and preferably in presence also of surface-active compounds, e.g. sodium alkylsulphonates. A suitable substratum, e.g. freshly precipitated barium sulphate, may also be present during coupling.

E. S.

Red Monoazo Pigments suitable for Automobile Finishes. DuP.

BP 693,598

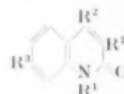
The manganese lakes of the monoazo compounds 4-halogeno(or nitro)anthranilic acid \rightarrow 2-hydroxy-3-naphthoic acid are deep red or maroon pigments. They have the advantage over known red pigments derived from arylides of 2-hydroxy-3-naphthoic acid, or from various diazotised halogeno-aniline(or -toluidine)sulphonic acids coupled with 2-hydroxy-3-naphthoic acid, of good stability in automobile finishes containing metallic (e.g. Al) flakes.

E. S.

Fluorescent Brightening Agents. Procter & Gamble Co.

USP 2,616,855

Carbostyryls of formula—



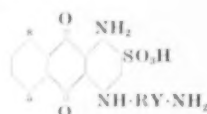
($R^1 = \text{H}$ or CH_3 ; $R^2 = \text{H}$, Alk, or aralkyl, of $<16^\circ\text{C}$; $R^3 = \text{OH}$, NH_2 , mono- or di-alkylamino, mono- or bis-hydroxyalkylamino, or heterocyclic amino, of $<7^\circ\text{C}$) are blue-fluorescing compounds suitable for adding as fluorescent brightening agents to alkaline detergents.

C. O. C.

Anthraquinone Derivatives—Direct Cotton Dyes. S.

BP 692,513

Compounds of formula—



($R =$ benzene or diphenyl nucleus; $Y = \text{H}$, CH_3 , C_2H_5 , O-CH_3 , $\text{O-C}_2\text{H}_5$, or SO_3H ; position 5, 6, 7, or 8 may carry SO_3H and position 6 and/or 7 halogen) condensed with a dihalide of general formula $\text{Hal-CO-CH}_2\text{-CA-CO-Hal}$ ($A = \text{H}$, Cl , Br , or CH_3 ; $\text{Hal} = \text{Cl}$ or Br) give green substantive dyes. Thus Na 1-amino-4-*p*-aminophenylamino-anthraquinone-2-sulphonate (2 mol.) is dissolved in water at 0°C., and fumaroyl chloride slowly added with sufficient aq. NaOH to maintain neutrality. The product—



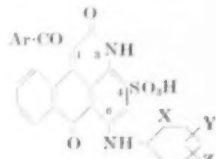
is salted out at 70°C.

R. K. F.

Anthrapyridone (3-Azabenzanthrone) Acid Dyes. S.

BP 692,902

Red acid dyes of formula—



($X = \text{CH}_3$ or C_2H_5 ; Y and $Z = \text{H}$, Hal , CH_3 , or C_2H_5) are prepared by condensing the corresponding 1-aminoanthraquinone derivative with an aryloxyacetic ester—
 $\text{Ar-CO-CH}_2\text{-COOAlk}$

Thus sodium 1-amino-4-(2:4:6-trimethylaniline)-anthraquinone-2-sulphonate is heated at 170–180° c. for 2 hr. with ethyl benzoylacetate in phenol containing potassium acetate.

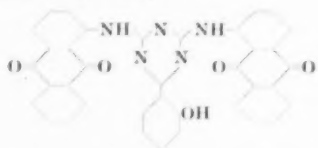
BP 692,970

Dyes of the same formula are made by condensing a 1-benzoyl-4:6-dihalogeno-2-hydroxy-3-azabenzanthrone with an appropriate aromatic amine and treating the product with an alkali-metal sulphite to replace the 4-halogen by SO_2H . Thus 1-benzoyl-4:6-dibromo-2-hydroxy-3-azabenzanthrone and 2:4:6-trimethylaniline are heated for 30 min. at 140° c. in presence of potassium acetate and CuSO_4 . The resulting product, after being separated by addition of ethanol and HCl , is heated under pressure for 16 hr. at 140° c. with 40% aq. K_2SO_3 and phenol.

R. K. F.

Hydroxyaryltriazine Vat Dyes. American Cyanamid Co. BP 691,506

Bisanthraquinonylamino-triazines containing an *o*-hydroxyaryl group are prepared by de-alkylating the corresponding alkoxy derivatives. Thus the greenish-yellow dye—



is made by suspending the methoxy derivative in nitrobenzene and passing HCl gas through at 135–200° c. The methoxy compound is prepared by a series of reactions as follows—Dicyandiamide is treated in acetone at 5–10° c. with KOH , and *o*-methoxybenzoyl chloride is added. The resulting product is converted to *o*-methoxybenzoylbisuret by heating with HCl , and then cyclised to 2:6-dihydroxy-4-*o*-methoxyphenyltriazine by treating with aq. KOH . Formation of 2:6-dichloro-4-*o*-methoxyphenyltriazine is effected by refluxing with PCl_5 and POCl_3 . This triazine is finally condensed with 2 mol. of 1-aminoanthraquinone.

R. K. F.

Triazine Vat Dye. American Cyanamid Co. BP 691,507
The 2:6-dichloro-4-*o*-methoxyphenyltriazine of BP 691,506 (see above) is heated at 105–110° c. in nitrobenzene with 1-amino-4-methoxyanthraquinone to give a bright red vat dye.

R. K. F.

Sulphuric Esters of Triazine Leuco Vat Dyes. American Cyanamid Co. BP 692,004

The triazine vat dyes of BP 691,506 and 691,507 (see above) are converted to leuco sulphuric esters by treating them with the addition product of SO_2 and *o*-picoline in presence of Fe . Thus the yellow vat dye 4-*o*-methoxyphenyl-2:6-bisanthraquinonylamino-triazine is stirred at 29–40° c. for several hours with the reaction product of chlorosulphonic acid and *o*-picoline in the presence of powdered Fe .

R. K. F.

1:2-Phthaloyl-6:7-benzacridone (Caledon Red BN). ICI. BP 691,118

The red vat dye 1:2-phthaloyl-6:7-benzacridone (C.I. 1162) is prepared by condensing 2-naphthylamine-1-sulphonic acid with 1-chloro- or 1-nitro-anthraquinone-2-carboxylic acid, use of the carcinogenic β -naphthylamine thereby being avoided. Thus 2-naphthylamine-1-sulphonic acid, 1-chloroanthraquinone-2-carboxylic acid, borax, and boric acid are heated in nitrobenzene, first at 115° c. and then at 200–210° c. for 2 hr. Any β -naphthylamine formed during the reaction is converted to a water-soluble derivative by adding monochloroacetic acid and heating for a further 2 hr. at 200–210° c. before separating the dye by cooling and filtering.

R. K. F.

Phthalocyanine Derivatives. ICI. BP 691,905

A chloromethylated phthalocyanine is condensed with a phenol to give products which are spirit-soluble, can be applied to cotton if alkali-soluble, can be coupled with diazotised amines, and can be sulphonated to give water-soluble dyes. If the phenol used is salicylic acid, they are chromable dyes. Thus, copper trichloromethyl-phthalocyanine, ZnCl_2 , and phenol are heated together at 120° c. for 3 hr.

R. K. F.

Phthalocyanine Vat Dyes. Basf. BP 692,383

Blue phthalocyanine vat dyes are made by heating together aromatic or heterocyclic *o*-dinitriles or *o*-dicarboxylic diamides with finely divided cobalt, or one of its compounds, in presence of carboxylic or sulphonic acids or their alkali-metal or NH_4 salts which are unsuitable for producing phthalocyanines. Thus phthalodinitrile, anhydrous CoCl_2 , and malonic acid are heated together until formation of the dye is complete.

R. K. F.

Non-crystallising Copper Phthalocyanine. General Aniline. USP 2,618,642

Copper phthalocyanine is rendered non-crystallising by mixing it with anhydrous trichlorobenzene, adding anhydrous aluminium chloride, and heating to 180° c. It is then filtered, and the residue freed from trichlorobenzene, treated with either aq. NaOH or HCl , boiled with live steam for a short time, filtered while hot, washed until neutral, and dried.

C. O. C.

Cyanine Dyes. Ilford. BP 693,623–4

Dyes of formula—

$$\text{X} \{ \text{R}^1 \text{N} [\text{CH} \text{---} \text{CH}]_n \text{C} \text{---} \text{CH} \text{---} \text{CH} \text{---} \text{CH} \text{---} \text{C} \text{---} \text{CH} \text{---} \text{CH} \text{---} \text{CH} \text{---} \text{C} [\text{CH} \text{---} \text{CH}]_m \text{N} \text{---} \text{R}^2 \}$$

(R^1 and R^2 = Alk or aralkyl; D^1 and D^2 = residues of 5- or 6-membered nuclei; n and m = 0 or 1) are excellent photographic sensitizers. Their synthesis and that of their intermediates are described.

C. O. C.

β -Carotene. Deutsche Hoffmann-La Roche. BP 693,259

2-Methyl-4-(2:6:6-trimethylcyclohex-1-enyl)but-2-en-1-al is condensed with a compound of formula $\text{HC} \text{---} \text{C} \text{---} \text{X} \text{---} \text{O} \text{---} \text{R}$ ($\text{X} = \text{C}(\text{CH}_3)(\text{OH})\text{---CH}_2\text{---}$ or $\text{---C}(\text{CH}_3)\text{---CH}_2\text{---}$; R = hydrocarbon radical) and the condensate converted by allyl rearrangement, and if desired partial hydrogenation of the triple bond, dehydration, and subsequent treatment with acid into 2:6-dimethyl-8-(2:6:6-trimethylcyclohexen-1-yl)octa-2:4:6-trien-1-al or -5:7-dien-3-yn-1-al respectively. Either of these compounds is condensed with a half-molecular proportion of "acetylene di-magnesium bromide" or lithium acetylide and, in any desired sequence, the C_{40} dihydroxy compound formed is dehydrated and hydrogenated with H_2 at each triple bond.

C. O. C.

Carbon Black. Phillips Petroleum Co. USP 2,616,794–5

A rapid method of producing carbon black from carbonaceous gases or vapours. It is very flexible, being readily controlled to yield soft, intermediate, or hard blacks as desired.

USP 2,617,714

When carbon black is made by spraying oil into a furnace, the yield can be increased if the degree of atomisation of the oil is increased and the size of the resulting droplets decreased by adding water to the hydrocarbons used.

C. O. C.

Carbon Black. Union Oil Co. of California.

USP 2,618,533

A method of making furnace black of particle size 10–20 μ .

C. O. C.

Rôle of Mordants in Fur Dyeing (VIII p. 353).

Interactions Between Organic Dyes and Polymers. I—Influence of Potassium Polyvinyl Sulphate on the Absorption Spectrum and Fluorescence of Rhodamine 6G in Aqueous Solution (VIII p. 353).

Photochemistry of the Bleach-out Process (IX p. 353).

V—PAINTS; ENAMELS; INKS

Dispersion Problems in Modern Media. W. Carr. J. Oil & Col. Chem. Assoc., 36, 246–256 (May 1953).

Most finely powdered materials such as pigments resist equally wetting by water and by oils, as the liquids cannot displace the air at the surface of the particles. To accomplish this, mechanical energy must be put into the system in the form of a grinding or milling process; this is assisted by the use of surface-active agents, which also reduce reaggregation. In the manufacture of dry distempers the pigment is dry-ground with filler and a water-soluble binding agent. Oil-bound distempers are produced by grinding the pigment paste into an oil-water emulsion, a process which does not materially affect the stability of the emulsion. The inclusion of a strong wetting agent prevents the transfer of pigment to the oil phase on prolonged

grinding, this leading to loss of colour value, particularly with Hansa yellows. Initial difficulties in the dispersion of organic pigments in emulsions of polyvinyl acetate have been overcome. In paint systems the pigment may (but does not usually) affect the film-forming properties, the degree and time of grinding required for dispersion, the storage behaviour of the paint, and those rheological factors which control flow and brushability. The pigment manufacturer can modify a pigment for use in a given medium by the addition of fillers, diluents, and surface-active agents, to give suitable levels of required properties affecting the manufacture, storage, and application of paints. A method is described by which it may be demonstrated that rosin, added to pigments in order to improve their texture and to lower their oil absorption, is actually adsorbed on to the pigment surface. Though the rosin is added in the form of its K or Na salt, it is adsorbed strongly enough to resist removal in the washing and filtration which follow. The method is based on the increase in surface tension resulting from the removal (by adsorption) of rosin molecules from the surface of a saturated soln., and gives an approx. measure of the extent of the adsorption. Results obtained with seven organic and four inorganic pigments are tabulated and discussed. Reference is made to BP 626,695, which describes the preparation of pigments in forms which can be incorporated into paint vehicles merely by stirring. The pigmentation of lacquers presents many of the problems which exist with paints; in addition, the comparatively low concn. of pigment is insufficient to produce false body, and soft pigments of very small particle size and low sp. gr. are required to avoid settling out during storage. With printing inks, the flow properties are of paramount importance, storage being unimportant, since such inks are made up as required. For the pigmentation of waxes for various finishes, mineral oil is necessary to secure satisfactory dispersion. The production and advantages of flushed pigment pastes are described; they are not much used in Britain, the diversity of demand making them uneconomical to produce.

J. W. D.

Pigmentation of Latex Paints. L. A. Melsheimer and W. H. Hoback. *Ind. Eng. Chem.*, **45**, 717-725 (April 1953).

In the manufacture of latex paints in which water is the continuous phase, care must be taken to avoid flocculation or agglomeration of the binder and/or pigments prior to application, e.g. due to overcrowding at any stage of manufacture. Pigments which are poorly dispersed or which tend strongly to flocculate do not develop full colour value, and may cause streaking and unevenness. Low electrolyte content and pH > 7 are essential to emulsion stability. Casein (usually as the ammonium salt) is an excellent dispersant for pigments, extenders, and organic toners, it improves the dispersion properties of the aq. phase, and it is effective as a protective colloid, stabiliser, and thickener. Anionic agents assist greatly in wetting the pigment and in securing min. liquid requirement. Experimental evidence is presented to illustrate the value of liquid absorption titrations in determining the best dispersing and wetting agents to use in manufacturing a given paint, and the proportions in which to use them. All pigments used must be properly dispersed and mutually compatible (with the latex also) in order to obtain max. colour value and stability. Considerable experimental evidence is quoted in illustration of the principles stated. There are 15 references to the literature.

J. W. D.

Effect of Pigments on the Drying Times of Conjugated Unsaturated Oils. J. D. von Mikusch and K. Mebes. *Dtsch. Farben-Z.*, **7**, 1-6 (1953); *Chem. Abstr.*, **47**, 3580 (10 April 1953).

The drying rates of 0.05 mm. thick paint films on glass were compared, the comparisons being based on 10 ml. lacquer linseed oil (I) or an isomerised linseed oil (II) of 50% conjugation, bodied to 3.8 poises at 20°C. The paints contained turpentine (0.4 ml.), mineral spirits (0.8), 10% Pb naphthenate (0.2), 2% Mn naphthenate (0.05), 3.3% Co naphthenate (0.05) (0.2% Pb, 0.01% Mn, 0.0165% Co), and pigment (10 g.). The dust-free and tack-free drying times (hr.) for I and II paints containing various pigments were—no pigment 7, 14; I, 2; Pb₂O₃ 8, 12; 1.5, 2.5; Signal Red, Fe-free 8, 16; 2.5, 4; cinnabar 8, 16; 3, 5; Chrome

Yellow 8, 16; 3, 5; TiO₂ "E" 9, 16; 4, 6; lithopone, Red Seal, 10, 16; 4, 6; Chrome Green 9, 17; 3, 7; lithopone, Silver Seal, 10, 16; 6, 10; Ultramarine 10, 17; 7, 12; Zinc Yellow 10, 16; 10; 16; red iron oxide 10, 16; 16, 24; Zinc Green 12, 20; 16, 24; Prussian Blue 26, 45; 26, 48; Manganese Violet 40, 48; 48, —; black iron oxide 20, 26; 48, —; i.e. the effect of Manganese Violet or black iron oxide is much more pronounced in the case of II paint (48:1) than with I paint (40:7). Pigments containing Zn, Mn, or Fe are particularly unfavourable with II; this resembles the previously observed inhibitor action of excess Mn or Zn driers. The drying times of six pigments were studied in wood oil (III) and ricene oil (IV), a dehydrated castor oil, with the increased drier content of Pb 0.3, Mn 0.02, and Co 0.033%—no pigment I 7, 16, II 1, 1.5, III 0.5, 0.75, IV 3, 6; Pb₂O₃ 1.7, 12, II 1, 1.5, III 0.5, 0.75, IV 3, 6; Signal Red I 7, 16, II 1.5, 2, III 0.75, 1, IV 4, 7; Chrome Yellow I, 8, 16, II 1.5, 3, III 1, 1.5, IV 4, 7; Lithopone, Red Seal, 1.8, 16, II 2, 3.5, III 1, 2, IV 5, 12; Zinc Yellow I 10, 16, II 5, 8, III 3, 7, IV 8, 16; Zinc Green I 10, 16, II 5, 9, III 3, 7, IV 18, 5. Thus all three conjugated oils are more affected by pigments than I, and particularly by those containing Zn. The effect increases with the conjugation of the oils (75-80% in III, 45-50% in II, 25-30% in IV, 0 in I). Thus the drying times of III, II, IV, and I paints pigmented with Zinc Green are 9.3, 6, 3, and 1 times that of the unpigmented paint; with Zinc Yellow the ratios are 9.3, 5.3, 2.66, and 1. As the two Zinc Green series show, the amount of driers used affects the drying time of different oils differently. Numerous drier combinations were therefore tried for various pigments in I and II, and optimum combinations of Pb, Co, and Mn were selected. With I 0.2% Pb + 0.015% Co + 0.01% Mn is best for lithopones, Zinc White, TiO₂, Chrome Yellow, Zinc Yellow, and red iron oxide; 0.4 Pb + 0.032 Co + 0.02 Mn for Chrome Green, black iron oxide, Prussian Blue; 0.3 Pb + 0.02 Co + 0.02 Mn for Zinc Green; 0.6 Pb + 0.1 Co + 0.03 Mn for Manganese Violet; and 0.016 Co + 0.01 Mn for white lead and Pb₂O₃. With II 0.2 Pb + 0.01 Mn is best for white lead, TiO₂, Chrome Yellow, and Chrome Green; 0.5 Pb + 0.04 Mn for Lithopone, White Seal, and Zinc White; 0.4 Pb + 0.015 Co for Lithopone, Red Seal; 0.15 Co for Zinc Yellow or Zinc Green; 0.2 Pb + 0.01 Co for Pb₂O₃; 0.5 Pb + 0.04 Co + 0.01 Mn for red or black iron oxide; 0.6 Pb + 0.04 Mn for Prussian Blue; and 0.1 Co for Manganese Violet. Paints made with II by using these driers and pigments dry dust-free in 1-3 hr. and tack-free in 1.5-6.0 hr., the corresponding times for I paints being 6-16 hr. and 12-30 hr.

C. O. C.

Reflectivity of Aluminium Pigment and Paint.

G. M. Babcock and F. B. Rothwisch. *Paint, Oil, Chem. Rev.*, **115**, (24), 53 (1952); *Chem. Abstr.*, **47**, 5131 (25 May 1953).

Measurement (with a Hunter goniophotometer and a modified Hunter hazemeter) of the reflectivities of regular, diffuse, and specular types of Al pastes show that regular and/or diffuse pastes have better all-round reflectivity characteristics than specular pastes, diffuse pastes are "whiter" and/or "brighter", and specular pastes are darker and more mirror-like in character.

C. O. C.

PATENTS

Aqueous Dispersions of Pigmented Alkyd Resins.

Commonwealth Engineering Co. of Ohio, BP 693,188

An aqueous suspension of a pigment is added to a saponified oil or a fatty acid. The precipitate is separated and added to a partly condensed reaction mass of glycerol and phthalic anhydride. The whole is then emulsified in water, a mixture of β -ethoxyethanol and ammonium caseinate being used as the emulsifying agent. The product is used as a coating composition.

C. O. C.

Printing Ink Vehicle. Sun Chemical Corp., BP 693,785

Inks containing as vehicle a polyglycol solution of an N-alkoxymethylpolymethylene polyamide of the type described in BP 573,482 (J.S.D.C., **62**, 123 (1946)), in which $\pm 10\%$ of the amide groups are substituted by alkoxymethyl groups, yield highly glossy prints when either air-dried or steam-set.

C. O. C.

Rapid-setting Inks. W. H. Smith & Son, BP 692,024

Coatings or inks which set rapidly (<30 sec.) in presence of an acidic gas, e.g. sulphur dioxide, comprise a partial condensation product obtained by mixing, with cooling, furfuraldehyde or a liquid polymer thereof (3-4 parts) and

an arylenediamine, e.g. 2,4-tolylenediamine (I), together with a plasticiser, a resin, and pigments. The products are useful as carbon-paper coatings and printing inks. E. C.

Inks for Application to Plastics and Waxy Surfaces. USP 2,618,574

Inks containing a hydrocarbon polymer or interpolymers, especially a chlorinated or chlorosulphonated ethylene polymer or interpolymers, are particularly suitable for application to plastics or waxy surfaces. C. O. C.

Red Monoazo Pigments suitable for Automobile Finishes (IV p. 349).

VI—FIBRES; YARNS; FABRICS

Protein Model. S. Mizushima, T. Shimanouchi, M. Tsuboi, and T. Sugita. *J. Chem. Soc. Japan, Pure Chem. Sectn.*, **73**, 624-626 (1952); *Chem. Abs.*, **47**, 3635 (25 April 1953).

A model based on combination of the *E* (extended) and *B* (bent) forms is suggested and compared with Pauling and Corey's spiral model. The suggested model, like all those hitherto proposed, has adequate interatomic distances and valency angles, but unlike the others also has correct X-ray periodicity, and the positions for internal rotation correspond closely to the potential minimum of internal rotation. This agrees with the fact that the hindering potential for rotation is generally greater than the energy of the hydrogen bond, whereas Pauling and Corey's model corresponds to a potential maximum of internal rotation about the CO-CHR bond as axis. C. O. C.

Surface Areas of Proteins. V—Mechanism of Water Sorption. J. M. Seehof, B. Keilin, and S. W. Benson. *J. Amer. Chem. Soc.*, **75**, 2427-2430 (20 May 1953).

Sorption of water by solid proteins is characterised by evolution of heat, a peculiar hysteresis, swelling, and increase in the B.E.T.* surface area. Heat evolution is of the order of magnitude of the heat of vaporisation of water, and in conjunction with the poor thermal conductivity of the protein slows sorption considerably. The hysteresis is unusual in that it is almost constant over the whole range of partial pressures p/p_0 from about 0.05 to 0.90 and is independent of temperature. Although the hysteresis loop is quite reproducible in both branches, the sorption-desorption curves do not correspond to states of thermodynamic equilibrium, and thermodynamic data calculated from them are apt to be most anomalous. The surface areas of proteins as measured by the B.E.T. method show a reproducible increase after sorption of water, and can be interpreted in terms of particle dimensions to give an apparent molar density for water which is anomalously high and indicates rather unusual packing efficiency in the solid. Probably hysteresis is associated with bonding on the free basic groups of the protein. Existing data on sorption show excellent correlation between the number of free basic groups and the maximum amount of hysteresis. Sorption seems to be initially surface adsorption of water, followed (even at low relative pressures) by rather quick diffusion of water molecules into the interior of the molecule, where the most strongly bonding sites are the free basic groups in the side-chains. This internal diffusion is accompanied by progressive swelling of the structure, increase of the binding to these active centres, with concomitant weaker adsorption on to the polypeptide skeleton, and finally at high pressures multimolecular adsorption equivalent to solvation, eventually leading to solution. If this is so and the swelling process is irreversible, the hysteresis is accounted for, and if the cooperative action of the swelling should have affected principally the binding by the free basic groups, then the constancy of the hysteresis is also accounted for. Such a hypothesis seems reasonable and consistent with all the known facts on the sorption process. C. O. C.

* Brunauer—Emmett—Teller

Digestion of Wool by Insects. VII—Some Features of Digestion in Three Species of Dermestid Larvae and a Comparison with *Tineola* Larvae. D. F. Waterhouse. *Australian J. Sci. Research, B5*, 444-459 (1952); *Chem. Abs.*, **47**, 3998 (25 April 1953).

Examination under polarised light of wool in the digestive tracts of *Anthonomus australis*, *Anthonomus verbasci*, and *Attageus piceus* showed that many fibres disintegrated as they passed down the gut. The pH of the midgut was ca.

7.0 and the redox potential -190 to -230 mv. The highly reducing conditions in the dermestid midgut reduced the disulphide bonds of wool keratin; this permitted attack by proteolytic enzymes. Most of the cysteine thus produced was not degraded further, and was excreted. Dermestid larvae did not produce metal sulphides after injection of appropriate salts. The faeces remained of normal colour except when a coloured cysteine-metal (Co) complex or reduction product (Te) was formed. But in *Tineola* larvae part of the cysteine was degraded further by a process partly chemical (high pH) and partly enzymic (desulphhydrase, splitting off H_2S). Neither dermestid nor *Tineola* larvae were able to digest the water-insoluble fraction (fibroin and sericin C) of silk. C. O. C.

Polystyrene Monofilaments and Bristles. K. J. Cleereman, H. J. Karan, and J. L. Williams. *Modern Plastics*, **30**, (9), 119, 120, 122, 124, 126, 128, 130, 132, 134, 136, 196-201 (May 1953).

Physical properties are a complex function of orientation and the portion of the retardation-time spectrum oriented. These two factors are functions of the fabricating variables—% hot stretch, temperature of stretching bath, rate of stretch, and rate of quench. Generally speaking, the following procedures result in the production of good polystyrene monofilaments—(i) Stretch at 250-270% (ii) Stretch to slightly below the maximum % hot stretch. This gives products of optimum physical properties. Excessive stretching results in milky fibres of very low knot strength. (iii) Stretch at a high rate. (iv) Quench at a moderate rate. Too rapid quenching prevents the short-relaxation-time chains from becoming disoriented and induces thermal strains in the extruded filament. These two factors lower heat stability. Quenching at a moderate rate partly anneals the filaments. (v) Anneal the filaments. This improves heat stability and straightens the fibres with no deterioration in physical properties. C. O. C.

PATENTS

Regenerated Keratin Fibres. Courtaulds. BP 692,876
Keratin is treated with aq. H_2O_2 in presence of $FeSO_4$ and an acid, the resulting oxidised keratin dissolved in aq. alkali, and the solution extruded into an aq. coagulating bath. C. O. C.

Fibre-forming Linear Polyethers. Courtaulds. BP 693,980

Linear polyethers having fibre-forming properties are obtained by reaction of equimolecular proportions of a dihydric phenol and a disulphonic ester of a diol in presence of alkali, the molecular proportion of which is at least twice that of the disulphonic ester. C. O. C.

Linear Polyamides from Dinitriles and Form-aldehyde. Monsanto. USP 2,617,786

Polymers of formula $[CO-R-CO-NH-CH_2-NH]_x$ (R = a bivalent aliphatic hydrocarbon, oxahydrocarbon, or thiahydrocarbon radical; x = whole number) are obtained by condensing bifunctional nitriles with formaldehyde. They have fibre-forming properties. C. O. C.

Solvent for Acrylonitrile Spinning Solutions. Monsanto. BP 692,782

A mixture of nitromethane and water is an excellent solvent for copolymers of < 86% of acrylonitrile and > 14% of a vinyl ester of a monocarboxylic acid of < 7°C, e.g. vinyl acetate or propionate. C. O. C.

Ternary Acrylonitrile Copolymers. American Viscose Corp. BP 693,864

Ternary polymers containing by wt. 70-84% of acrylonitrile, 1-10% of a vinyl-substituted heterocyclic tertiary amine, and 6-20% of methacrylonitrile have much greater affinity for acid dyes than copolymers containing only acrylonitrile and the tertiary amine in the above proportions. C. O. C.

Stabilised Acrylonitrile Polymers. Monsanto. USP 2,617,783

Addition of acids of boron and esters thereof to acrylonitrile polymers improves their resistance to thermal discoloration.

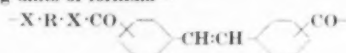
USP 2,617,784
The combined use of an aluminium salt and maleic acid or anhydride or an ester thereof gives greater stability than does either used separately. C. O. C.

Fluorescent Fibre-forming Linear Polymers.

California Research Corpn.

BP 693,375

Fluorescent fibre-forming linear polymers containing recurring units of formula—



(R = alkylene, cycloalkylene, arylene, or aralkylene of 2–16 C; X = NH or O) are produced by reaction of a suitable stilbenedicarboxylic acid derivative with a compound of formula HO-R-OH, H₂N-R-NH₂, or H₂N-R-OH. They have better dyeing properties and resistance to heat than hitherto known linear polymers prepared from dibasic acids and glycols or diamines.

C. O. C.

Soluble Yarns and Threads of Partly Carboxymethylated Cotton (X p. 354).

VII—DESIZING; SCOURING; CARBONISING; BLEACHING**Some Factors Influencing Foam Stability.**Sporek. *J. Amer. Oil Chem. Soc.*, **30**, 190–193 (May 1953).

It is believed that liquid films owe their stability to the Gibbs elasticity. How this elasticity may arise is discussed, and it is concluded that in some cases a non-equilibrium value may be the important factor. Some data on surface composition from radiochemical experiments and foam fractionation are presented. An explanation of the origin of the slow and fast draining films of Ross, Miles, and Shedlovsky is offered.

P. G. M.

VIII—DYEING

Rôle of Mordants in Fur Dyeing. V. A. Pehelin and N. V. Grigoreva. *Legkaya prom.*, **11**, (11), 32–34 (1951); *Chem. Abs.*, **47**, 5121 (25 May 1953).

Oxidation of *p*-diphenylenediamine and *p*-aminophenol and also of a mixture of *p*- and *m*-phenylenediamines and pyrocatechol with H₂O₂ in presence of K₂Cr₂O₇, CuSO₄, and FeSO₄ results in products having similar light-absorption curves. The mordants had little influence on the fastness to light of the dyes; with dichromate there was a slight decrease in fastness.

C. O. C.

Interactions between Organic Dyes and Polymers.

I—Influence of Potassium Polyvinyl Sulphate on the Absorption Spectrum and Fluorescence of Rhodamine 6G in Aqueous Solution. M. Koizumi and N. Mataga. *J. Chem. Soc. Japan, Pure Chem. Sectn.*, **73**, 814–816 (1952); *Chem. Abs.*, **47**, 5797 (25 June 1953).

The changes in absorption spectra and in fluorescence intensity occurring when varying amounts of K polyvinyl sulphate are added to aq. soln. of Rhodamine 6G are discussed in the light of metachromasy.

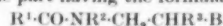
C. O. C.

PATENTS**Vat Dyeing.**

Lankro Chemicals.

BP 692,942

Better levelling is obtained if the vat contains one or more non-ionic high-mol.wt. protective colloids and 0.0025–0.1% of a cationic surface-active amine-amide salt, the cationic part having the formula—



(R¹ = Alk, alkenyl, aralkyl, or aralkenyl of 8–20 C; R² = H, Alk, or aralkyl; R³ = H or Alk; B = primary, secondary, or tertiary organic nitrogen base or ammonia).

C. O. C.

Dyeing Protein Fibres.

Wolsey.

BP 692,924

Protein fibres acquire greatly increased affinity for acid dyes in solutions of pH > 3 if they are first treated with a non-tertiary alcohol of < 5 C in presence of an acid catalyst.

C. O. C.

Coloration of Cellulose Ester or Ether Fibres.

BrC.

BP 692,934

Excellent colorations of very good fastness to rubbing are obtained with little or no saponification of the fibre by application of an aqueous dispersion containing an unreduced vat dye, an aldehyde-sulphoxylate, a hydroxy-alkylamine, and a thiocyanate, followed by steaming and reoxidation.

C. O. C.

Continuous Diazotype Dyeing and Printing.

L. E. Ravich.

USP 2,616,803

The material is treated with a solution of a photosensitive dye intermediate and then with a solution of a coupling component, neither the intermediate nor the component being soluble in the solvent used for the other. The treated material is exposed to light, and then treated with alkali so as to produce an insoluble dye in the exposed portions.

C. O. C.

Simultaneously Dyeing and Saponifying Cellulose Acetate Staple Fibre.

Canadian Celanese.

USP 2,616,779

A mixture of < 2% by weight of cellulose acetate staple fibre and a dye liquor containing a saponifying agent is passed through an enclosed passage as dyeing and saponification occur. Very uniform dyeings are obtained.

C. O. C.

Fluorescent Brightening Agents. I—Quantitative Determination of Dyeing Characteristics (IV p. 346).

Fading of Dye Solutions by Ultrasonics. III—Relation between Ultrasonic Fading and Light Fading (XIV p. 356).

IX—PRINTING**Adsorption of Carbocyanines by Gelatin.**

H. O. Dickinson.

Colloque Sensibilité phot. (Paris, 1951); *Science et Inds. phot.*, **23A**, 103–110 (1952); *Chem. Abs.*, **47**, 4773 (25 May 1953).

Study of the absorption spectra of a series of carbocyanines of similar structures, dissolved in dil. soln. of gelatin, indicates that the mode and the degree of adsorption of dye by gelatin depend on at least three factors—dye structure, concentration of gelatin, and pH. Some simple carbocyanines derived from benzothiazole do not seem to be adsorbed in the aggregated state; some prepared from substituted benzothiazoles have a great tendency to show the *J* absorption band, associated with aggregation, and sometimes also a narrow *H* band, of much shorter wavelength. At certain concentrations of gelatin the dye is not adsorbed at pH values below the isoelectric point. Adsorption may be sufficient to provoke precipitation of gelatin-dye complexes when the dye is in the *J* or *H* state.

C. O. C.

Adsorption of Sensitising Dyes in Photographic Emulsions.

W. West, B. H. Carroll, and D. H. Whitecomb.

J. Phys. Chem., **56**, 1054–1067 (1952); *Chem. Abs.*, **47**, 4772 (25 May 1953).

Many sensitising cyanine dyes are adsorbed on the grains of photographic emulsions according to the Langmuir equation, the molecules in the saturated monolayer being oriented with their planes parallel and projecting away from the surface at an average intermolecular distance of ca. 4.6 Å. Less well adsorbed dyes often show discontinuity between adsorption as isolated molecules and a cooperative phase having different spectral characteristics. Poly-layer adsorption occurs also, and merocyanines conform to Langmuir or approximately Freundlich curves according to their class. Non-planar dyes are feebly adsorbed compared with planar dyes. Heats of adsorption determined from the Clausius-Clapeyron equation are about 10–12 kg.cal./mole for the first additions of well adsorbed cyanine dyes in silver halide-gelatin emulsions, and decrease with increasing surface coverage. Both electrostatic and van der Waals forces are active in the adsorption of cyanines, while some kind of linkage between Ag⁺ and double-bonded S acts in the case of some merocyanines. Although some correlation between adsorption and sensitising efficiency appears with some dyes, in general they are not parallel properties. The inefficient optical sensitisation of non-planar dyes cannot be explained by their low absorptivity, nor is supersensitisation caused by any material increase in the strength of bonding of the sensitizer to the silver halide in presence of the supersensitizer.

C. O. C.

Photochemistry of the Bleach-out Process.

A. Polgar.

Z. wiss. Phot., **46**, 188–237 (1951); *Chem. Abs.*, **47**, 5283 (10 June 1953).

No single type of chemical reaction explains the photobleaching of dyes—oxidation, reduction, isomerisation, and photolytic decomposition are found among different dye classes. The well known acceleration of photobleaching

by anethole, which may depend on formation of an anethole peroxide, often shows an optimum concentration, deviation from which in either direction reduces sensitisation. Acceleration of photobleaching by allylthiourea also involves oxidation of the dye. Dyes of the quinone-imine, acridine, azine, thiazine, triphenylmethane, diphenylmethane, and xanthene groups respond to allylthiourea as a sensitizer, as do azo dyes containing thiazole or pyrazole nuclei. Certain indo- and thio-carboaniline dyes are highly sensitive in presence of allylthiourea. Photobleaching is subject to failure of reciprocity between time and intensity; the sensitometry of the process is complicated by an "afterdarkening" phenomenon associated with production of coloured as well as colourless products. Numerous graphs are given showing the dependence of bleaching on the initial concentrations of dye and sensitizer, the effect of dye mixtures, and the sensitometric characteristics (gradient and Schwarzschild index) of the bleaching process. C. O. C.

PATENTS

Pigment Coating Compositions. Imperial Paper & Color Corp. USP 2,616,861

Stable aqueous pigmented pastes, prepared by incorporating a dispersed pigment in an aqueous solution of a cationic resin in presence of an anionic protective colloid, yield prints of good fastness to washing, light, rubbing, and smudging. C. O. C.

Photomechanical Colour-corrected Separation Prints. A. V. Jonsson. BP 693,555

A method of obtaining a satisfactory corrected half-tone colour-separation print for use in multicolour printing with little or no need for retouching the transparencies used to make the print. C. O. C.

Stain-preventing. Short-stop Bath for Photographic Azine Dye Images. General Aniline. USP 2,618,559

Stains arising from air oxidation of 2:4-diaminoaniline developers are readily eliminated by treating the developed multilayer colour film with an aqueous short-stop bath containing 0.5-5.0% of a pyruvic acid. C. O. C.

Developing Electrostatic Images with Electroscopic Powder. Battelle Development Corp. BP 693,905

An electrostatically charged developing powder is applied to an electrostatically charged insulating layer supported on a conductive plate, this layer constituting the image. A charge opposite to that of the layer and the same as that of the powder is induced on the areas of the plate not covered by the layer so as to repel the powder from those areas. C. O. C.

Colour Photography. B. Gaspar and P. D. Dreyfuss. USP 2,616,806

Passive stabilised diazo compounds (see Saunders, K. H., *The Aromatic Diazo Compounds and their Technical Applications*, London, 2nd edition 1949, p. 71) are used in the bath, being converted into active compounds capable of coupling during development of the photographic material. C. O. C.

Automatic Application of Transfers to Glass, Ceramics, and the like. Johnson, Matthey & Co. BP 694,177

Coloration of Cellulose Ester or Ether Fibres (VIII p. 353). Continuous Diazotype Dyeing and Printing (VIII p. 353).

X—SIZING AND FINISHING

Preservation of Fishing Nets, Trawl Twines, and Fibre Ropes for Use in Sea Water. W. R. G. Atkins and F. J. Warren. *J. Marine Biol. Assoc. United Kingdom*, 31, 509-513 (1953); *Chem. Abs.*, 47, 6145 (25 June 1953).

Immersion tests on cotton netting showed that treatment with Al stearate in white spirit and Cu naphthenate (Cuprinol) gave best results, the best lasting for 9 months compared with 22 weeks for the untreated. C. O. C.

Microfiltration with Resin-impregnated Wool Filters. E. D. Kane. *Ind. Eng. Chem.*, 45, 860-864 (April 1953).

Electrolytic Interaction of Nylon with Aqueous Sodium Hydroxide at Different Temperatures

F. T. Wall and P. M. Saxton. *J. Phys. Chem.*, 57, 370-375 (1953); *Chem. Abs.*, 47, 6146 (25 June 1953). Adsorption of NaOH by nylon 66 fibres was studied at 25, 36.4, and 49.7°C., and equilibrium constants were determined for the adsorption, which occurred in two stages. The heats of reaction for the first stage were -12,900 and -12,600 g.cal. and for the second -9,900 and -9,600 g.cal. Equations were developed to relate the heat of adsorption with the change in [OH⁻] necessary to keep the amount of base adsorbed at different temp. constant. C. O. C.

PATENTS

Protecting Cellulose Fibres from Heat Ageing. United States Rubber Co. USP 2,616,822

Guanidine salts of acids of ionisation constant $\geq 1.75 \times 10^{-5}$ effectively impart to cellulose fibres resistance to deterioration when heated for long periods, guanidine carbonate being particularly effective when used as a boiling 10% aqueous solution, e.g. by immersing the cotton in it for 2 min. C. O. C.

Treating Non-woven Cellulosic Fabrics with Urea Resin Colloids. American Cyanamid Co. USP 2,617,744

Application of cationic aminotriazine-aldehyde resin acid colloids, e.g. an acetic-acid colloid of methylated trishydroxymethylmelamine, increases the tensile strength of non-woven cellulosic fabrics in which the fibres are all oriented in the same direction. C. O. C.

Soluble Yarns and Threads of Partly Carboxymethylated Cotton. U.S. Secretary of Agriculture. USP 2,617,707

Cotton and regenerated cellulose may be rendered soluble in water or dilute alkali while remaining insoluble in strong alkali and retaining their fibrous structure by carboxymethylation with liquors containing <50% of water, as much of the excess alkali as possible being removed by mechanical means and the remainder then being neutralised with acetic acid in an aqueous soln. of a water-miscible organic solvent, there being <60% of the solvent in the soln. C. O. C.

Rendering Textiles Water-repellent by Treatment with Emulsified Paraffin Wax and a Urea or Thiourea Precondensate. Nico ter Kuile & Zonen. BP 692,900

Modification of BP 606,788 (J.S.D.C., 65, 43 (1949)), improved and more durable water-repellency being obtained if the paraffin wax emulsion contains a hydrolysed protein as an emulsifying agent. C. O. C.

Mothproofing. Merck & Co. USP 2,617,747

NN'-Bischloroacetamidomethane gives excellent protection against clothes moths and carpet beetles when 0.25-1.0% on the wt. of wool is present. It is most conveniently applied from solution in an organic solvent. C. O. C.

Non-woven Fabric. International Cellulocotton Products Co. BP 693,711

A fabric formed of fibres held together by adhesives is stretched so as to amplify its porosity. The fabric embodies several strips of an adhesive material which becomes stronger when stretched. C. O. C.

Preventing Accumulation of Electrical Charges on Photographic Film, Paper, or Leather. Kodak. BP 693,975

If the metal rollers of a coating machine are interspersed with rollers covered with cloth which has been treated with an alkali-metal or ammonium salt of an aldehyde-naphthalenesulphonic acid condensate, e.g. Tamol NNO, then charges of static electricity which accumulate on the film, etc. are dissipated slowly, so that they do not cause discharge markings in the coating. C. O. C.

Simultaneously Dyeing and Saponifying Cellulose Acetate Staple Fibre (VIII p. 353). Rendering Cellulosic Fibrous Sheets non-adherent to Organic Solids (XI p. 355).

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Use of Cellulose Nitrate Lacquers and Emulsions in Paper Coating. J. J. Creasy. *World's Paper Trade Rev.*, 139, 87, 88, 90, 91, 93, 94, 96 (March 1953).

A review of the preparation and properties of cellulose nitrate coatings and their use in obtaining various finishes. Ten working recipes are given. C. O. C.

Carbonyl Oxycelluloses. W. M. Corbett, J. Kenner, and G. N. Richards. *Chem. and Ind.*, 462 (9 May 1953).

An addendum to a previous note (*Chem. and Ind.*, 154 (1953)—cf. *J.S.D.C.*, 69, 177 (May 1953)). The α -unsaturated carbonyl compound initially produced by alkaline degradation of disaccharides is rapidly converted to saccharinic acids and may be isolated in that form. The procedure should be of use in exploration of the chain structure of polysaccharides. W. R. M.

PATENTS

Nitrogen-containing Thermosetting Resins and Wet-strength Paper produced therewith. Monsanto. BP 694,330

A nitrogen-containing thermosetting resin suitable for wet-strengthening paper products is made by causing 1 mol. of urea to react with 2-4 mol. of formaldehyde in aq. soln. at pH 7.2-8.5 and 50-70°C. to form a hydroxymethylated urea; adding to the resulting solution 0.05-0.5 mol. of a water-soluble salt of an amino- or an amino-hydroxy-benzene- or -naphthalene-sulphonic acid containing no other substituents, an aliphatic amino mono- or di-carboxylic acid of 1-6 C, a water-soluble salt of such aliphatic acid, or an addition compound of such aliphatic acid or salt with formaldehyde; concentrating the resulting solution to 55-65% solids content (by wt.) without materially changing the degree of polymerisation of the hydroxymethylated urea; bringing to pH 4.5-5.5; allowing the hydroxymethylated urea and the added organic acid, salt, or addition compound to react and condense, at above 80°C. but below the boiling point of the solution, until the viscosity of the solution at 60% resin solids content is 5-10 poises measured with the Gardner-Holdt bubble viscometer; and finally adding a water-soluble base until the solution is sufficiently alkaline to minimise further increases in its viscosity. The addition product specified may be that of glycine or aspartic acid and formaldehyde; the mono-carboxylic acid, glycine; and the aromatic water-soluble salt, the Na salt of sulphanilic acid, of 8-amino-1-naphthol-3:6-disulphonic acid, or of 1-naphthylamine-3:6:8-trisulphonic acid. Wet-strength paper is prepared by adding the resin together with an acid or alum to the pulp stock, forming the sheet of paper, and heating the formed sheet. The amount of resin added may range from 0.25 to 5%, preferably 1-3%, by weight of resin solids, based on the bone-dry weight of pulp. S. V. S.

Paper Coating. Hercules Powder Co. USP 2,616,818

A copolymer of >50% of acrylamide with <50% of another acrylic compound is used as the adhesive in aqueous suspensions of clay or pigment used for coating paper. The coated paper has high brightness, smoothness, and gloss and a good finish and feel after calendering. C. O. C.

Rendering Paper Transparent. R. R. Parmentier. USP 2,616,815

The paper is treated with a mixture of mineral oil (10-35% by vol.), toluene (4-10), and carbon tetrachloride (55-80). Seepage of the composition from the paper is prevented by aftertreating with a mixture of wax (2-6% by vol.), petroleum hydrocarbons (31-47), and carbon tetrachloride (47-67). C. O. C.

Alginate-sized Diazotype Paper. General Aniline. USP 2,617,727

Replacement by sodium alginate of some or all of the starch used for the surface sizing of diazotype paper results in improved evenness of penetration of the sensitising chemicals, and as the dye components have greater affinity for sodium alginate than for starch, the visual intensity of the dye is increased, resulting in sharper, clearer, and better defined images. C. O. C.

Rendering Cellulosic Fibrous Sheets non-adherent to Organic Solids. Dow Corning. BP 693,788

Cellulosic fibrous sheets are rendered water-repellent, greaseproof, and extremely non-adherent to normally

adhesive materials by treating them with a dispersion of a liquid of formula $(CH_3)_3H_2SiO_{(4-a-b)/2}$ ($a = 1.0-1.5$; $b = 0.75-1.25$; $a + b = 2.0-2.25$) in an aqueous solution of a cellulose ether. The dispersion contains 0.1-20% by weight of the above liquid and 0.1-10% of the cellulose ether. C. O. C.

Preventing Accumulation of Electrical Charges on Photographic Film, Paper, or Leather (X p. 354).

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Acetylation of Collagen. R. W. Green, K. P. Ang, and L. C. Lam. *Biochem. J.*, 54, 181-187 (May 1953).

In mildly alkaline suspension collagen is acetylated by acetic anhydride at the free amino groups. The number of N-acetyl groups introduced is equal to the total number of lysine and hydroxylysine residues found by analysis. Dry collagen does not react with cold acetic anhydride, but in the presence of acetic acid or of small amounts of water both N- and O-acetylation take place, the reaction being slow. P. G. M.

Rôle of the Amino and the Hydroxyl Groups of Collagen in Chrome Tanning. R. W. Green. *Biochem. J.*, 54, 187-191 (May 1953).

Acetylation of either free amino or free hydroxyl groups of collagen causes a marked diminution in its ability to take up either cationic or anionic chromium complexes from solution. For chromic sulphate solutions, this effect has been studied over a wide range of basicities and for differing degrees of acetylation. It is most pronounced at high basicity, and increases almost linearly with the degree of acetylation. The experimental results suggest that, while the initial reaction between the chromic complex and collagen occurs at the carboxyl groups of the latter, the coordination of amino or hydroxyl radicals is essential to the formation of a stable compound. In the basicity range normally employed in industrial chrome tanning, approximately one collagen amino or hydroxyl group in every three appears to be involved in the reaction. P. G. M.

New Mechanism in Chrome Tanning. I. P. Strakhov. *Lezgaya prom.*, 11, (12), 23-25 (1951); *Chem. Abs.*, 47, 5149 (25 May 1953).

The theory of the trans effect indicates that coupling of chrome compounds by collagen is greater when half of the coordination points in the inner sphere of the chromium belong to more active transradicals than water. Work described shows that cationic compounds of basic chromic sulphate used in tanning, which have a greater number of labile molecules, have a greater capacity for combining with albumins than have cationic chromic chloride and anionic chromic sulphate. C. O. C.

Chemistry of Oil Tanning. I—Formation of Peroxide Groups in the Oil. J. Glavind and J. W. Pedersen. *Acta Chem. Scand.*, 6, 451-453 (1952); **II—Chemical Nature of the Bonds between Peroxidised Fats and Collagen.** *Ibid.*, 453-456; *Chem. Abs.*, 47, 5707 (10 June 1953).

I—Work on fish oils sampled during the tanning of sheepskins confirms that peroxide formation plays a decisive rôle in oil tanning.

II—The peroxides formed in oil tanning are effective only at pH < 5.5. Skin and oil-tanned leather were analysed for total N and free amino N. About 0.14 millimole of fatty acid is taken up per gram of dry leather, so that the leather contains 4.2% oil. The free amino groups change only from 0.38 millimole/g. skin to 0.35 millimole/g. leather; thus these groups cannot be involved in the tanning reaction. Fat peroxides (or hydroperoxides) are known to react with organic acids, and an analogous reaction may occur in oil tanning, leading to fatty acid-collagen linkages of ester character. Saponification of tanned hide liberates 0.31 millimole of carboxyl groups per gram of leather, indicating that one molecule of unsaturated fatty acid combines with two carboxyl groups. The leather was detanned during saponification. Apparently the hydroperoxides form bridges between carboxyl groups of adjacent collagen peptide chains. C. O. C.

Nylon-coated Leather. F. Leonard, T. B. Blevins, W. S. Wright, and M. G. DeFries. *Ind. Eng. Chem.*, **45**, 773-775 (April 1953).

The application of a solubilised nylon to leather to be worn next to the skin of amputees is described. Tests are detailed, the results of which show that the nylon-coated leather is far superior to uncoated leather in resistance to abrasion, flexing, water, perspiration, tensile stress, and water vapour permeation. Field tests show that the nylon coating has a profound effect in arresting the deterioration of harness during use. The nylon soln. remain stable for ~ 3 days, but may be stabilised for periods of several months by compounds such as phenol, picric acid, and lactic acid, which contain loosely bound hydrogen atoms. J. W. D.

Preventing Accumulation of Electrical Charges on Photographic Film, Paper, or Leather (X p. 354).

XIII—RUBBER; RESINS; PLASTICS

Solvents for Polyacrylonitrile. E. E. Walker. *Chem. and Ind.*, 320-322 (1953).

Discussion on paper in *J. Appl. Chem.*, **2**, 470 (1952) (cf. J.S.D.C., **68**, 539 (Dec. 1952)). Solvent power is not governed solely by the cohesive energy densities (C.E.D.) of the solvent and the solute, as is especially apparent when the action of mixed solvents on polymers is considered. The affinities between the three pairs of components in such a ternary system exert an influence, and the heat of dilution of the system is a more satisfactory means of assessing solvent power. The latter may be derived in terms of the C.E.D. of the components and the affinity between them when this is of dipolar character. Where high affinities are present, e.g. owing to hydrogen bonding, these cannot be accurately accommodated mathematically. From the expression for heat of dilution the following inferences are made—where special affinities are absent, the heat of dilution and hence the solvent power are determined solely by the C.E.D. of the mixed solvents; where the C.E.D. of the three components are equal or where that of the polymer lies between those of the solvents, and the two solvents show low affinity (barely miscible), the mixture shows good solvent action on the polymer. With polyacrylonitrile, nitromethane (a non-solvent) gives solvent mixtures with a number of hydrogen-bonded compounds, most of which are themselves non-solvents, e.g. water, formic acid, formamide, or dichloroacetic acid. The molecular size of the solvent does not appear to be important in determining solvent power. E. C.

PATENTS

Patterned Plastic Films. New Wrinkle. *BP* 692,888

The film is coated with a solution of a resin or resin-like substance and then locally heated, so that the areas where heat is applied become covered with a soft skin which wrinkles when treated with water, after which water is applied to the coating. C. O. C.

Plasticiser-Accelerator for Amino Resins. Fran. *BP* 692,452

Salts of an organic base, e.g. hexamine, with the acid monoester obtained from a dibasic acid, e.g. oxalic acid, and a monoether of a polyol, e.g. α -glyceryl phenyl ether, function both as accelerators and as plasticisers for amino resins. E. C.

XIV—ANALYSIS; TESTING; APPARATUS

Separation and Determination of Mixtures of Chlorinated *o*-Cresols. F. Freeman, K. Gardner, and D. W. Pound. *J. Appl. Chem.*, **3**, 160-164 (April 1953).

The separation of the chlorination products of *o*-cresol is described. The procedure for preparing the pure chloro-*o*-cresols is outlined, and the development of a rapid method for estimating the four cresols appearing in the chlorination product is traced. It consists in separating, by partition chromatography on kieselguhr, the mixture into two fractions—6-chloro-*o*-cresol + 4,6-dichloro-*o*-cresol, and *o*-cresol + 4-chloro-*o*-cresol. The

components of these fractions are estimated differentially by ultraviolet spectrophotometry. Results are shown for the analysis of mixtures of the pure cresols. J. W. D.

Determination of Dyes in Lipsticks, Face Paints, Ointments, and Brilliantines by Chromatography with Alumina Discs. J. Deshusses and P. Desbaumes. *Mitt. Gebiete Lebensmittel. und Hygien.*, **43**, 501-504 (1952); *Chem. Abs.*, **47**, 5076 (25 May 1953).

The dyes in cosmetic fats can be separated by Mottier and Poterat's method (*Chem. Abs.*, **46**, 7942 (1952)) by using chromatography with alumina discs. C. O. C.

Electro-osmotic Investigation of the Structure of Pigments and other Extremely Thin Layers. J. K. Wirth and W. Machu. *Werkstoffe und Korrosion*, **3**, 444-453 (1952); *Chem. Abs.*, **47**, 4691 (25 May 1953).

A description of apparatus for determining the sign of the electric charge on pigments and for electro-osmotically investigating other very thin layers. It permits determination of the size and the number of pores, the total cross-sectional area of the pores, the ζ potential, the distance between pores, etc. C. O. C.

Fading of Dye Solutions by Ultrasonics. III—Relation between Ultrasonic Fading and Light Fading. T. Azami and T. Hinohara. *J. Chem. Soc. Japan, Pure Chem. Sect.*, **73**, 713-715 (1952); *Chem. Abs.*, **47**, 5121 (25 May 1953).

Fading by light of a dilute aqueous solution of dye is paralleled by that resulting from the action of ultrasonic vibration, and it may be possible to work out a method of utilising ultrasonics to test the fastness of dyes to light. C. O. C.

Radiochemical Method for the Micro-estimation of α -Amino Acids separated on Paper Partition Chromatograms. S. Blackburn and A. Robson. *Biochem. J.*, **54**, 295-299 (May 1953).

A radiometric method is described for the micro-estimation of amino acids separated on one-dimensional paper chromatograms. They are converted to their copper complexes with copper phosphate containing ^{64}Cu ; 1 μg . of α -amino nitrogen can be estimated with an accuracy of $\pm 3\%$, and 2 μg . of α -amino N and above with an accuracy of $\pm 2\%$. Analyses of isoleucine, valine, and arginine in salmine sulphate are reported. P. G. M.

Identification of Peptide End-groups as Dimethyl-amino Acids. V. M. Ingram. *J. Biol. Chem.*, **202**, 193-201 (May 1953).

Tetramethyl-L-ornithine and dimethyl-DL-isoleucine have been prepared by reductive methylation, using formaldehyde and hydrogenating in the presence of a palladium catalyst. Dimethylamino acids can be identified by paper chromatography. Reductive methylation of peptides, followed by hydrolysis and paper chromatography, has been employed to determine the amino end-group as the dimethylamino acid. Glycyl, alanyl, leucyl, phenylalanyl, glutamyl, and prolyl peptides have been examined by this method. P. G. M.

PATENTS

Optically Measuring the Thickness of Transparent Sheets. Celanese Corp. of America. *BP* 693,804

Measuring Colour or Opacity of a Fluid. Candy Filter Co. *BP* 692,675

The fluid flows through a container having opposed windows, through which light can be directed through the fluid on to a light-sensitive device. Each window is formed in part by a transparent disc, which can be rotated so that the area covering the window can be constantly changed and cleaned. C. O. C.

Formation of Methine Bridges by the Action of Formamide. I—Trimethincyanines. II—Oxonols. III—*mero*-Cyanines (IV p. 343).

Fluorescent Brightening Agents. I—Quantitative Determination of Dyeing Characteristics (IV p. 346).

Nitrogen-containing Thermosetting Resins and Wet-strength Paper produced therewith (XI p. 355).

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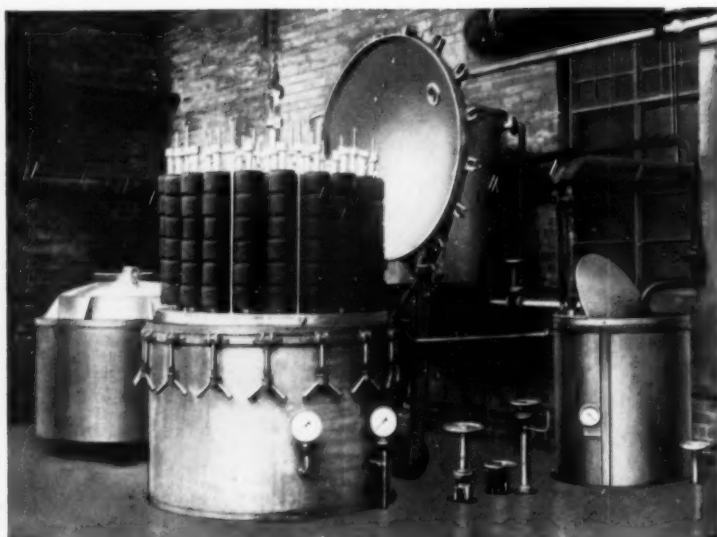
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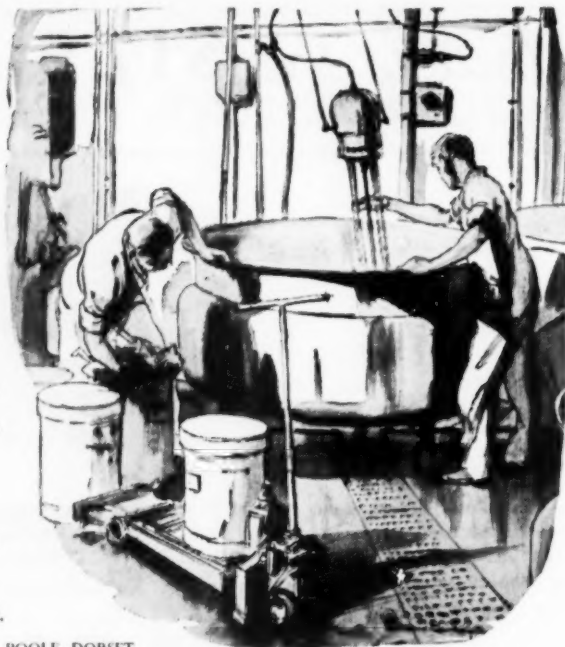
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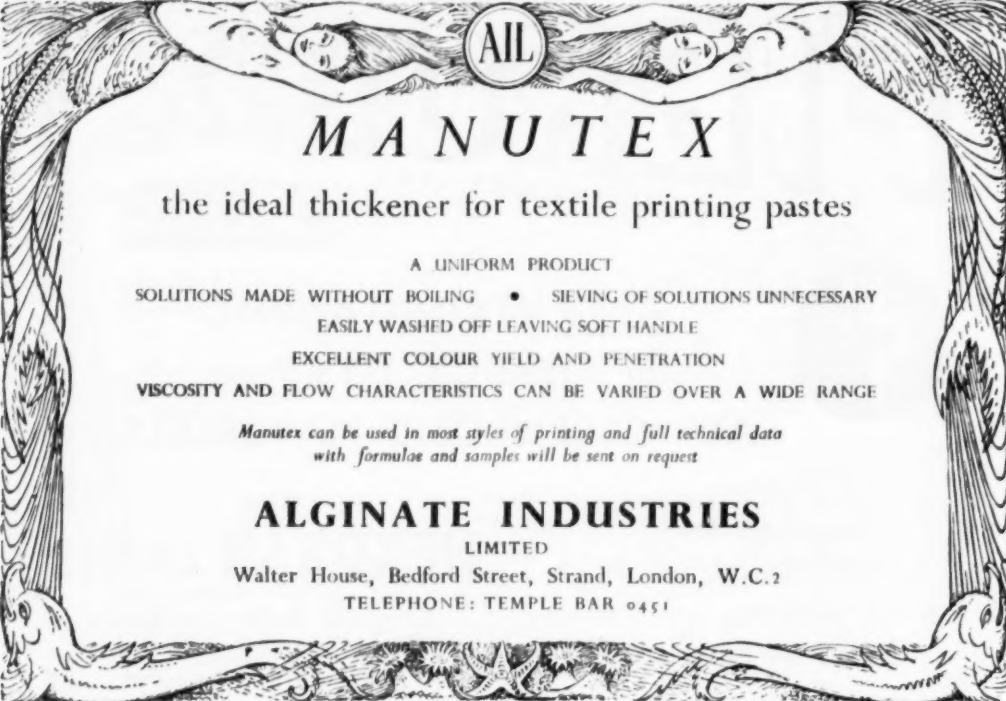
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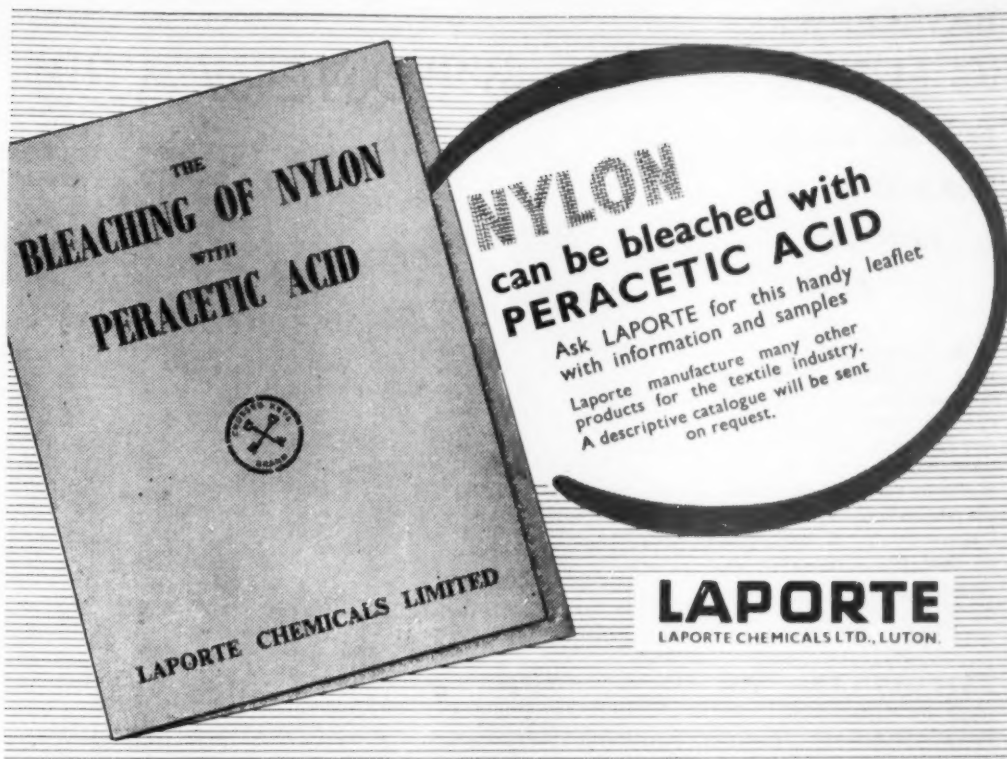


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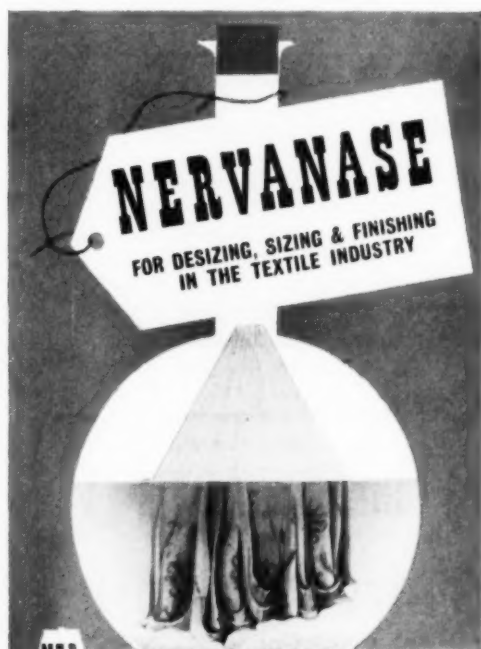


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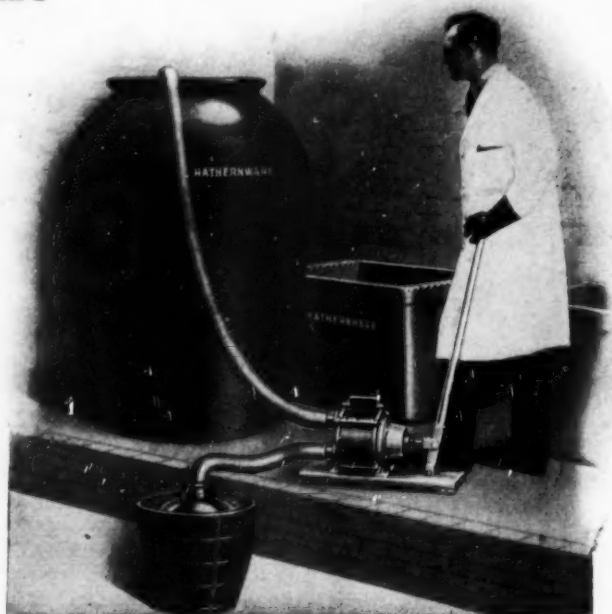
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